APPENDIX A

SELECTION OF PRODUCTS FOR CHAMBER TESTING

The document shown in this Appendix was prepared during the course of Research Project 93-315, and served as the basis for a portion of the project. However, the main body of this report should be consulted as the most complete and final presentation of the study activities and results.
SELECTION OF PRODUCTS FOR CHAMBER TESTING

for

DETERMINATION OF FORMALDEHYDE AND TOLUENE DIISOCYANATE EMISSIONS FROM INDOOR RESIDENTIAL SOURCES

CALIFORNIA AIR RESOURCES BOARD
PROJECT NO. 93-315

prepared by

T. J. KELLY
BATTelle
505 KING AVENUE
COLUMBUS OH 43201-2693

Revised: March, 1995
SELECTION OF PRODUCTS FOR CHAMBER TESTING

1. INTRODUCTION

This document reports the rationale and results of the selection of HCHO and TDI sources for chamber testing. The aim of this effort was to select a reasonable cross-section of samples from all the likely categories of indoor residential HCHO and TDI sources. The selection of samples was weighted so that more samples were selected for testing from the most important source categories, and fewer from less important categories. Weighting of sample selection was made as quantitative as possible, by comparing the various potential source categories on characteristics such as emission rate, loading rate in a home, or potential for exposure during use of the product. An extensive information gathering effort was conducted as the basis for product selection. Not unexpectedly, information on HCHO products was far more abundant than information on TDI products. As a result, the product selection process for HCHO was much more detailed than for TDI.

It is important to note that the product categories considered for HCHO in this study excluded combustion sources. Such sources, which include gas ovens and ranges, gas space heaters, kerosene space heaters, and smoking, may be significant indoor HCHO sources. However, they are the subject of other CARB studies, and were not addressed here. Secondary formation of HCHO indoors, by reactions of organic emissions with ozone from outside, also was not considered. This source of HCHO indoors has only recently been suggested. Although emissions from some products such as carpet may lead to secondary formation of small amounts of formaldehyde, this process is not considered a key source of HCHO indoors.

The information gathering effort that led to the selection of products relied on literature surveys, reviews of reports and other documents, telephone inquiries to government and industrial representatives, and formal written requests for information. Not all of these inquiries resulted in receipt of useful information. In the descriptions presented in the following sections, no attempt has been made to document all the
activities of the information survey. In most cases only those contacts that resulted in useful information are cited and summarized.

In subsequent sections of this document, separate product selection efforts are described for HCHO and TDI. The former includes brief summaries of the information obtained for each of several product categories, as well as a final compilation and ranking of product information.

2. FOCUS ON THE CALIFORNIA MARKET

The intent of this study is to assess indoor HCHO and TDI emission rates from products and materials found in California residences. As a result, products to be tested will be obtained in California, from sources and locations where the products are moving through the marketplace into California homes. In identifying products for testing, information specific to use of the products in California residences was sought. However, information specific to California generally was not found. In general, data were available only on a regional basis. For example, recent information on wood products used in new home construction is segregated only on a regional basis, into North, East, and West areas of the country.\(^1\) Production and shipment data for major wood products\(^2\) are similarly segregated; the West region consists of all states west of the Rocky Mountains. Contacts with manufacturers of various product categories considered here disclosed the same results, that sales and/or use data were generally not available on a state-by-state basis. This information survey used the western regional data, where available, in lieu of California data.

This survey also found that the composition of most products sold in California is essentially the same as elsewhere in the country, because of the nature of the marketplace. For example, wood products industry sources indicated that sheet material sold for construction purposes is a commodity that moves throughout the country, i.e., the products sold in California are likely to be the same as those sold elsewhere.\(^3,4\) Thus the California market is not unique for those products. The same is true for the great majority of product types considered. However, for a few specific products, items sold in California may differ from those sold elsewhere. Industry
sources\(^{3,4}\) stated that finished items such as kitchen cabinets may differ somewhat from those sold elsewhere in the country, due to the styles and mix of materials used. Such differences are probably not large, but in any case products and component materials to be tested are to be obtained from the California market. A more significant difference may be in paints and other coatings, for which California regulations on volatile organic compound (VOC) emissions have led to different formulations for the California market. All samples to be tested will be obtained in the California marketplace, to assure that any composition characteristics unique to California will be accounted for.

3. HCHO PRODUCTS

A variety of HCHO-containing products were suggested as likely indoor emission sources in the RFP issued by CARB for this project. Battelle staff reviewed those categories, and also considered others based on previous experience. The following are summaries of the information obtained on each category. Note that when emission rate data are stated in the following, they refer to test conditions reasonably representative of residential conditions.

3.1 Wood Products

Wood products made of particles, chips, or layers of wood held together by HCHO-containing resins are without a doubt the most extensively studied sources of HCHO in homes. In gathering information for this product selection process, published reports of wood product testing were reviewed, and direct contacts were made with representatives of the wood products industry. This survey disclosed that the identities and uses of wood products in residences are numerous, and furthermore that substantial changes have occurred over the last several years in terms of the quantities of various products used, and the emission rates of those products. Changes have occurred due to regulatory pressure and voluntary industry initiatives to reduce HCHO emissions. Consumer preferences have also changed, altering the mix of wood products now found
in residences. In selecting products for this study, the emphasis was on representing the current state of wood product use. As a result, recent data on production, use, emission rates, and residential loadings of wood products were emphasized.

3.1.1 General

Before summarizing the information on residential loadings and emission rates, a general discussion of the types of wood products considered here is worthwhile. This study is primarily concerned with composite wood products used indoors in residences, because that use constitutes the most direct route for HCHO emission and residential HCHO exposure. For wood products used both in interior and exterior applications, the extent of interior use of those products was considered.

The wood products considered in this study can be broadly categorized by the type of resin used in their manufacture. Products manufactured with urea-formaldehyde (U-F) resins are subject to degradation by moisture, and so are used essentially exclusively for indoor applications. These products have generally been considered to be the most important indoor HCHO sources.\(^5\) The broad category of U-F products is sometimes referred to as interior wood products or non-structural panel products.\(^1,3\) The main product types among U-F wood products are particleboard, hardwood plywood, medium density fiberboard, and hardboard.\(^1,3\) Further subdivisions exist within these product types. For example, particleboard products include industrial particleboard, underlayment, and mobile home decking.\(^2\) Hardwood plywood consists mainly of plywood, but also includes prefinished panelling. However, use of the latter product has declined drastically due to changed consumer tastes over the past several years,\(^6,7\) and it is no longer a major indoor wood product, even in mobile homes. The category of non-structural panels may also include products made with melamine-formaldehyde (M-F) or other resins. These products generally occupy a small portion of the market, and release HCHO more slowly than do U-F products.

The other broad category of wood products consists of those made primarily with phenol-formaldehyde (P-F) resins, and suitable for exterior use. Such products are commonly referred to as structural or exterior panel products. These products share the
characteristic that the resin is much more stable than U-F resins, and so less prone to HCHO release. Important product types within the broad P-F category include oriented strand board (OSB), softwood plywood, and exterior particleboard. A product called waferboard, essentially a randomly-oriented predecessor to OSB, has been essentially completely replaced by OSB due to the latter’s greater strength. Production of waferboard has long since stopped in the U.S., and has nearly stopped in Canada, so that product was not included in this product selection.

A considerable amount of information is available on the use of wood products as construction materials in residences. However, much of the U-F material present in homes is not used as a bulk construction material, but is incorporated as a component of furniture, shelving, or cabinets. This is particularly true for medium density fiberboard, industrial particleboard, and stock hardwood plywood. In some cases, such as in kitchen cabinets, all of these materials may be present in the same item. This complicates the determination of separate product emission rates, especially since some products, such as MDF, are not used to a significant extent other than as a component of finished items. The implication for this product selection is that complete consumer items or at least finished components of such items, and not merely bulk sheet material, may be the form of in-home HCHO source pertinent to some wood products.

In this product selection process, the likelihood of obtaining wood products of widely differing emission rates was investigated. For example, comparison of material that did not meet existing emission standards set by HUD or ANSI to material that meets those standards would be of interest. However, discussions with industry representatives indicated that essentially no U.S.-made material is marketed anymore that does not meet such standards. As an example, ANSI chamber emission standards of 0.2 ppm and 0.3 ppm exist for particleboard flooring products and for standard industrial board, respectively. Many particleboard manufacturers simply make their products to meet the more stringent standard, regardless of use. As a result, of the 4.24 billion square feet of U-F particleboard produced in 1993, over half met the 0.2 ppm standard, and over 97 percent met the 0.3 ppm standard. Furthermore, the distributions of emission characteristics of the two product types (industrial board and flooring) overlap extensively, indicating that there is no sharp distinction between the
two products. The small amount of particleboard that exceeds these standards may come largely from "captive" production facilities that feed directly into manufacturing of finished items. Such material occupies a very small portion of the market, and in any case would be difficult to track in finished products. As a result, "non-HUD" material is not planned as a separate item for product selection.

Imported wood products are not subject to the U.S. production standards for HCHO release, and the product acquisition effort described in Section 5 of this report includes such products to the extent possible. However, imported wood products occupy only a small portion of the U.S. market. For example, total imports of particleboard and MDF products in recent years have about equalled total exports, and have been about 10 percent or less of total U.S. production.\(^2\) Specialty hardwood plywoods are generally imported due to cost considerations, but those products do not comprise the bulk of hardwood plywood found in residences. As a result, domestically produced wood products were the primary focus of this selection process, since they dominate the residential market.

Consideration was also given to whether "low-emitting" and "regular" grades of U-F wood products might be sold in the marketplace, and could be compared in this study. Such distinctions are apparently no longer made.\(^3\) Some manufacturers may have marketed "low-emitting" products at one time, by virtue of adoption of improved resins or production techniques, however, those approaches soon became so widespread in the industry that any competitive advantage disappeared. In actually purchasing products for testing in this study, attention will be paid to any advertising claims about the products, but a real distinction between various grades of product emissions is not likely.

3.1.2 Summary of Data

The information available on production, loading rates, and emission rates of wood products is much more extensive than that for any other category of products. Recent information in these areas is summarized in Tables 1-3. This information is
used in condensed form for establishing the number of products to be tested, in Section 3.10.

Tables 1a-1c summarize some recent information on the production of key U-F wood products. This information is presented to roughly indicate the relative quantities of materials going into residences.

Table 1a shows that industrial particleboard is by far the predominant U-F wood product. Most of this material ends up in residences in the form of cabinets, furniture, shelving, and other items. Board thicknesses of 5/8 in. and 3/4 in. each account for about one-third of current production of industrial particleboard. Floor underlayment and mobile home decking are the next two largest categories of particleboard production. For both these products, 5/8 in. is the most common board thickness produced. In general, these data indicate that the amount of U-F particleboard found in a home in the form of secondary products (such as cabinets, etc.) will likely be much higher than the amount used directly in flooring.

Table 1b indicates that MDF is produced nationally in quantities about one-third of those for industrial particleboard. MDF is used entirely in secondary products such as cabinets. MDF is distinguished primarily by product thickness; Table 2 shows that nearly 75 percent of all MDF produced is from 1/2 to 3/4 in. thick.

Table 1c shows that various forms of hardwood plywood occupy substantial shares of the market. Nearly all of such products are incorporated into cabinets, shelves, trim, etc., rather than used in bulk as flooring in homes. Stock plywood in 3/4 in. thickness is the single most common product. Table 1c also shows that hardwood plywood panelling is a small part of the current plywood production. The data in Table 1c may overestimate the actual production of veneer and panelling products in square feet, because the estimates shown assume a value per square foot for those products equal to that for stock plywood.

Table 1 does not include production data for U-F hardboard. Such information is not released by the American Hardboard Association.

Table 2 shows reported values of in-home loading rates for the wood product categories. All loading rate values are in square meter of product per cubic meter of home volume (m²/m³). To the extent possible, the loading rate data are broken down.
TABLE 1. RECENT PRODUCTION DATA ON U-F WOOD PRODUCTS

a: Particleboard\(^{(a)}\)

<table>
<thead>
<tr>
<th>Product Type</th>
<th>1993 Shipments, in Millions of Square Feet, 3/4-In. Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Particleboard</td>
<td>3,374</td>
</tr>
<tr>
<td>Floor Underlayment</td>
<td>284</td>
</tr>
<tr>
<td>Mobile Home Decking</td>
<td>167</td>
</tr>
<tr>
<td>Shelving</td>
<td>89</td>
</tr>
<tr>
<td>Door Cores</td>
<td>143</td>
</tr>
<tr>
<td>All Others</td>
<td>184</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4,241</strong></td>
</tr>
</tbody>
</table>

b: Medium Density Fiberboard\(^{(a)}\)

<table>
<thead>
<tr>
<th>Thickness</th>
<th>1993 Shipments, in Millions of Square Feet</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/8 to 1-1/2 in. thick</td>
<td>121</td>
</tr>
<tr>
<td>1/2 to 3/4 in. thick</td>
<td>851</td>
</tr>
<tr>
<td>1/4 to 7/16 in. thick</td>
<td>101</td>
</tr>
<tr>
<td>Other thicknesses</td>
<td>87</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1,161</strong></td>
</tr>
</tbody>
</table>

c: Hardwood Plywood\(^{(b)}\)

<table>
<thead>
<tr>
<th>Product Type</th>
<th>Estimated 1992 Shipments, in Millions of Square Feet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stock Plywood</td>
<td>746</td>
</tr>
<tr>
<td>Hardwood Veneer</td>
<td>400</td>
</tr>
<tr>
<td>Other Plywood Products</td>
<td>300</td>
</tr>
<tr>
<td>Prefinished Panelling</td>
<td>150</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1,600</strong></td>
</tr>
</tbody>
</table>

\(^{(a)}\) From reference 2.

\(^{(b)}\) Estimated from reference 9, assuming equal value for all products per square foot of production.
<table>
<thead>
<tr>
<th>Product</th>
<th>Loading Rate by Residence Type (m²/m³)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CSF</td>
<td>MH</td>
</tr>
<tr>
<td><strong>U-F Products:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particleboard</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.43&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>0.43&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>0.43&lt;sup&gt;(b)&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.047&lt;sup&gt;(11)&lt;/sup&gt;</td>
<td>0.41&lt;sup&gt;(11)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>0.030&lt;sup&gt;(11)&lt;/sup&gt;</td>
<td>0.047&lt;sup&gt;(11)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>0.167&lt;sup&gt;(12)&lt;/sup&gt;</td>
<td>0.5&lt;sup&gt;(12)&lt;/sup&gt;</td>
<td>0.112&lt;sup&gt;(12)&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.118</td>
<td>0.033</td>
<td></td>
</tr>
<tr>
<td>0.010</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td>0.039</td>
<td>0.059</td>
<td></td>
</tr>
<tr>
<td>0.28&lt;sup&gt;(13)&lt;/sup&gt;</td>
<td>0.25&lt;sup&gt;(13)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>0.07&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>0.04&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>0.23&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>0.22&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>0.43&lt;sup&gt;(58)&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium Density Fiberboard</td>
<td>0.26&lt;sup&gt;(c)&lt;/sup&gt;</td>
<td>0.26&lt;sup&gt;(c)&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.26&lt;sup&gt;(58)&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardwood Plywood</td>
<td>0.95&lt;sup&gt;(d)&lt;/sup&gt;</td>
<td>0.95&lt;sup&gt;(d)&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.066&lt;sup&gt;(12)&lt;/sup&gt;</td>
<td>1.0&lt;sup&gt;(12)&lt;/sup&gt;</td>
<td>0.049&lt;sup&gt;(12)&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.091&lt;sup&gt;(11)&lt;/sup&gt;</td>
<td>0.92&lt;sup&gt;(11)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>0.25&lt;sup&gt;(11)&lt;/sup&gt;</td>
<td>0.30&lt;sup&gt;(11)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>0.066&lt;sup&gt;(13)&lt;/sup&gt;</td>
<td>0.16&lt;sup&gt;(13)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>0.066&lt;sup&gt;(9)&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;0.005&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>&lt;0.005&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>0.03&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>0.04&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>0.43&lt;sup&gt;(58)&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardboard</td>
<td>&lt;0.005&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>0.01&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 2. (Continued)

<table>
<thead>
<tr>
<th>Product</th>
<th>CSF</th>
<th>MH</th>
<th>MF</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-F Products:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oriented Strand Board</td>
<td>0.06(^{(1)})</td>
<td></td>
<td>0.03(^{(1)})</td>
<td>Flooring</td>
</tr>
<tr>
<td></td>
<td>&lt;0.005(^{(1)})</td>
<td>&lt;0.005(^{(1)})</td>
<td>Cabinets/Trim</td>
<td></td>
</tr>
<tr>
<td>Softwood Plywood</td>
<td>0.30(^{(1)})</td>
<td>0.23(^{(1)})</td>
<td>Flooring</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.01(^{(1)})</td>
<td>0.02(^{(1)})</td>
<td>Cabinets/Trim</td>
<td></td>
</tr>
</tbody>
</table>
| Exterior Particleboard    | \(
\begin{array}{c}
\approx 0 \end{array}\)
\(^{(c)}\) |       |       |                |

(a) CSF = conventional single family; MH = mobile home; MF = multi-family.
(b) Full theoretical loading for 100 percent floor coverage; stated in HUD test procedure.
(c) Loading level specified in ANSI standard for MDF; reference 10.
(d) Full theoretical loading for 100 percent wall coverage; stated in HUD test procedure.
(e) Existing data show little use of this product indoors. However, such use may be increasing as a means of reducing indoor HCHO exposures, due to suggestions made in official publications (e.g., see reference 43).
by housing type, wood product type, and product use (e.g., flooring, cabinets, furniture). The assumed loading rates employed in standard chamber tests for HUD compliance are included for U-F particleboard, hardwood plywood, and MDF.

Some qualifying comments are in order concerning Table 2. Wood products are produced in more than one thickness, and the surface area of material is generally adjusted to normalize to a common thickness when calculating a loading rate. For some of the cited loading rates in Table 2, the assumed thickness of product was not stated. Typical product thicknesses can be assumed, e.g., 5/8 in. and 1/2 in. for particleboard as underlayment and in cabinets, respectively; 1/4 in. for hardwood plywood in cabinets, etc. In most cases, the loading rates shown are for only those homes containing the product; i.e., the loading rates are not averages over a population of homes, some of which do not contain the product. Thus these loading rates are relevant to indoor HCHO exposure. However, the Anderson and McKeever report, although extremely useful in describing wood product use, does not allow isolation in all cases of subsets of homes in which individual products are used. Nevertheless, by careful combination of the various types of information presented, it was possible to derive reasonable loading rate estimates. The values indicated as coming from reference 1 in Table 2 are estimates based on wood product use, drawn from actual use data on large numbers of homes. However, it must be recognized that these values were calculated by Battelle from data in the report, and are not directly stated in the report. The loadings calculated from the wood products use data are reasonably comparable to the other data in Table 2.

In general, the data on wood products use show that as of 1988 indoor use of P-F products (primarily OSB and softwood plywood) was almost exclusively in floors. In flooring, softwood plywood use greatly exceeded that of OSB (see Table 2). An insignificant amount of these products is used in interior shear walls, and a very small amount in "millwork", including cabinets, moldings, countertops, etc. For U-F products, the situation is nearly reversed. As of 1988 millwork was by far the largest use of U-F products in the home, consuming 2.5 times as much material as used in floors, where U-F board was used primarily as underlayment (i.e., as the top layer in multi-layer flooring). Millwork is a particularly important use of U-F particleboard and
hardwood plywood, accounting for 67 percent and 98 percent, respectively, of the total indoor use of these products in new homes in 1988. Overall, the use of P-F materials in flooring in new homes in 1988 outweighed that of U-F materials by a factor of over 5. Conversely, the use of U-F material in millwork in 1988 was nearly 18 times as great as that of P-F materials. This factor excludes the substantial use of U-F products in furniture. These data show that the indoor uses of U-F and P-F wood products are quite distinct.

The data in Table 2 show that the loading rates of the key U-F products, particleboard and hardwood plywood, in home construction are generally much lower than the maximum theoretical rates assumed for standard chamber tests. This is especially true for hardwood plywood wall paneling. The use of this material has declined sharply over the past 10 years or so, due largely to consumer preferences. A large part of this decrease has been in mobile home manufacture, where gypsum wallboard has almost completely replaced plywood paneling. For example, a survey by the Manufactured Housing Institute in 1993 showed over 95 percent of manufactured homes built in 1993 used gypsum wallboard, but only 5 percent used hardwood plywood paneling. Similar low usage rates also apply in conventional homes. The important factor for this study is that to be realistic relative to in-home HCHO emissions, chamber tests of U-F products used in home construction should employ product loading rates well below the standard loadings used for compliance tests.

Table 2 also shows that for U-F products furniture, cabinets, and trim are likely to be the dominant loadings within a home. Furniture is a particularly important use for MDF and hardwood plywood. In the present study it will be imperative to obtain test samples that represent these final uses of U-F products.

Table 3 summarizes published HCHO emission rate measurements for wood products, in $\mu g/m^2$/day. It must be stressed that these values come from a variety of studies conducted with a range of test conditions. In a few studies the exact nature of the products tested (e.g., resin used) was not clearly stated. As a result, quantitative comparisons of individual test results may not be appropriate, however, the consensus of test results from each product type should give a reasonable basis for ranking.
<table>
<thead>
<tr>
<th>Product</th>
<th>Emission Rates (Reference) (µg/m²/day)</th>
<th>Measured</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-F Products:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particleboard</td>
<td>2,000 - 25,000(16,17)</td>
<td>1,500 - 12,900(19)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>168,000(18)</td>
<td>10,500(14)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,300 - 5,500(20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4,800 - 48,000(21)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>460 - 8,400(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium Density Fiberboard</td>
<td>17,600 - 55,000(22)</td>
<td>9,300 - 14,300(19)</td>
<td></td>
</tr>
<tr>
<td>Hardwood Plywood</td>
<td>14,000(16,17)</td>
<td>6,500(9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>68,000(18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardwood Plywood Panelling</td>
<td>1,500 - 34,000(16,17)</td>
<td>3,200(6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24,000(21)</td>
<td>2,000(9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>140 - 4,700(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardboard</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-F Products:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oriented Strand Board</td>
<td>&lt; 2,000(15)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Softwood Plywood</td>
<td>&lt; 2,000(15)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>240 - 720(23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt; 100(16,17)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exterior Particleboard</td>
<td>&lt; 2,000(15)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) To meet HUD 0.3 ppm chamber limit.

(b) To meet HUD 0.2 ppm chamber limit.
relative emission rates. For some products, HCHO concentration results in ppm are available from standard chamber test methods. In such cases, emission rates were calculated based on the test conditions of product loading and air exchange rate, using the relationship

\[ E_R = (C \cdot \frac{N}{L}) \cdot 24 \]

where
- \( E_R \) = HCHO emission rate in \( \mu g/m^2/day \)
- \( C \) = chamber HCHO concentration (generally reported in ppm and converted to mg/m\(^3\) using the conversion 1 ppm HCHO = 1.25 mg/m\(^3\) at 70°F and 1 atm)
- \( N \) = air exchange rate, in hr\(^{-1}\)
- \( L \) = product loading rate in m\(^2\)/m\(^3\), and
- 24 = conversion from hr\(^{-1}\) to day\(^{-1}\).

In all cases, the emission rates shown in Table 3 are primarily for comparison to those of other wood products or product categories.

Table 3 shows that the quantity of emissions data for U-F products is much greater than for P-F products, with the exception of U-F hardboard, for which no emissions measurements could be found. Hardboard is expected to have a much lower HCHO emission rate than other U-F products, because of the high temperatures and pressures used in its production. The reported and calculated emission rates for U-F products cover a considerable range, even for a single product type. However, nearly all the U-F product emission rates exceed those measured from P-F products. In fact, the most extensive review of P-F test results\(^{(15)}\) indicates that HCHO levels in chambers loaded with P-F products are often barely distinguishable from the chamber background levels. For this reason only an upper limit value is shown for the various emissions data reviewed in that study. It is important to note that current emission rates from U-F products are lower than those from several years ago. As a result, the lower end of the emission range of U-F products now overlaps that of P-F products, although in general the U-F emission rates are substantially higher.
3.2 Textiles

In the early 1980s, Pickrell et al.\(^{16,17}\) assessed the HCHO release rates of a variety of fabrics, including new clothes, draperies, and various upholstery fabrics, using very small static chambers. The observed emission rates from fabric products ranged from less than 1 µg/m\(^2\)/day to several hundred µg/m\(^2\)/day, with a substantial variation among samples of each type of product. In general, new, previously unwashed clothing had the highest emission rates among fabric products, ranging from 15 to 750 µg/m\(^2\)/day. Drapery fabrics produced somewhat lower HCHO emissions, and upholstery, latex-backed, and other fabrics produced the least, ranging in emission rates from less than 1 to 100 µg/m\(^2\)/day. The variability in fabric products was considerable; for example, one sample of latex-backed fabric gave emissions of 90-100 µg/m\(^2\)/day, while another similar product gave emissions of <1 µg/m\(^2\)/day. Possible explanations for this variability include different treatments of the fabric, or different product histories, i.e., previous exposure of the material to high HCHO levels.

Clothing, bed linens, and drapery material are the main fabric uses which incorporate permanent-press surface coatings in the home. Much recent work has been conducted by the textile industry on the chemistry of HCHO release from treated fabrics.\(^{24-27}\) This work has focused on the sorption of formaldehyde on cellulose, and the role of pH and humidity in the hydrolysis of the permanent-press coating. However, no realistic tests of formaldehyde release to air were conducted in those studies,\(^{24-27}\) and the information search disclosed no recent emission rate data for fabric materials.

Contacts with the American Textile Manufacturers Institute (ATMI) also produced no direct HCHO emission data, but did produce other information.\(^{28}\) The permanent-press resins currently used in the textile industry are formulated and pre-treated to produce much lower HCHO emissions than those used 10 or more years ago. Proper application and curing of the coatings can minimize HCHO release. The ATMI communication also indicates that the decay of HCHO emissions from textiles is very rapid, and that initial emissions are greatly reduced by washing of the fabrics.\(^{28}\) Emission of HCHO from textile products is apparently considered a negligible health hazard by the
CPSC, (28) and HCHO exposures from fabrics are said to be within the levels allowed under California's Proposition 65. (28)

The overall conclusion from this information is that in-home formaldehyde release from treated fabrics is probably small, but is maximized by the presence of new, unwashed fabrics. It is planned that new permanent-press clothing will be tested for HCHO release in this study both before and after washing.

3.3 Insulation Products

Actual emission measurements on insulation materials are scarce. The desiccator studies conducted by Pickrell et al. (16,17) for the CPSC indicated that fiberglass insulation materials had HCHO release rates comparable to those of new permanent press clothing, and equal to about 2 percent or less of those of various pressed wood products. Individual samples of six types of insulation products exhibited emission rates from 52 to 620 µg/m²/day, and there was reasonable agreement in average values among the six product types. (16,17) A single test of fiberglass insulation in a ventilated medium-sized chamber showed a release rate of 3,000 µg/m²/day, again about 2 percent of the value for particleboard in the same test. (16,18) More recently, Matthews and Westley (29) measured HCHO release from faced and unfaced fiberglass roll insulation, using both a "surface emission monitor" (SEM) and a small test chamber. In that study, conducted for the CPSC, emission rates of new products were found to be 26 to 53 µg/m²/hr (i.e., 620 to 1300 µg/m²/day) using the SEM. After one to three months, emission rates had decayed to about 10 to 25 µg/m²/hr (i.e., 240 to 600 µg/m²/day), as determined by both SEM and chamber tests. These results are consistent with the earlier studies. (16-18)

Modern insulation materials are made predominantly with P-F resins, which are less prone to HCHO release than are U-F resins. As a result, insulation products are not likely to be major contributors to in-home HCHO levels. (29) Furthermore, most insulation products are not directly present in the indoor living space; wall insulation and pipe insulation for example, are relatively separated from the living space. Only ceiling tiles are likely to be directly exposed to the living area. The temperatures to
which wall insulation is exposed may greatly exceed indoor temperatures, promoting HCHO emission, but the separation of that product from the indoor space will reduce the impact of any such emissions.

### 3.4 Carpet

In the desiccator studies by Pickrell et al.,\(^{(16,17)}\) carpet samples produced the lowest HCHO emissions of any of the product categories tested. The maximum formaldehyde release rate from any carpet sample was 65 μg/m\(^2\)/day, and nearly all samples exhibited release rates of less than 10 μg/m\(^2\)/day.\(^{(16,17)}\) These rates were less than 0.2 percent of the corresponding rates from wood products in those tests. A single test of carpet in a medium-sized ventilated chamber indicated a rate of about 1,500 μg/m\(^2\)/day; this value was less than 1 percent of the value from particleboard in the same chamber.\(^{(16,18)}\) Although carpets are known to release a wide variety of organic chemicals into indoor air,\(^{\text{e.g.},30,32}\) in general formaldehyde is not considered a significant emission. Contacts with the carpet industry in this study indicated that HCHO is no longer used in the manufacture of carpet, and this was confirmed by Dr. Bruce Tichenor of U.S. EPA,\(^{(33)}\) who indicated that carpet is not a source of HCHO to indoor air.

The most extensive study of carpet emissions appears to be that by the CPSC\(^{(30,31)}\) which evaluated emissions of dozens of chemicals from several varieties of carpet. That document also reports that HCHO is no longer used in carpet manufacture. In tests conducted by Lawrence Berkeley Laboratory in the CPSC study,\(^{(30,31)}\) HCHO emissions were detected only from "hard-back" carpet, which accounts for only about 2 percent of the carpet market, and is used predominantly in schools and offices rather than in homes. The HCHO emission from that product decayed very rapidly, i.e., by about 90 percent in one week. These results indicate that residential formaldehyde emissions from carpets are likely to be negligible.\(^{(30,31)}\)

Although direct emissions of HCHO from carpets appear to be unimportant, a variety of other chemicals are emitted, and may affect indoor air quality. Weschler et al.\(^{(32)}\) have shown that ozone present in indoor air may react with unsaturated
hydrocarbons emitted from carpets to produce HCHO and other aldehydes. The impact of this process depends on the indoor ozone concentration and the level of reactive organics in the home. Weschler et al.\(^{(32)}\) point out that other products containing unsaturated hydrocarbons may also react with ozone indoors, e.g., rubber, linoleum, waxes, oils, lubricants, air fresheners, and untreated wood. The possible indirect formation of HCHO indoors by this process is not the subject of the present study, but may be a significant source of HCHO in some residences, in areas where outdoor ozone levels are high enough to result in significant indoor ozone concentrations.

### 3.5 Paper Products

Emission of HCHO from some paper products is suspected because of the use of U-F resins to provide wet strength and other desirable properties to paper and paperboard. However, measurements of HCHO release from paper products are rare. Pickrell et al.\(^{(16,17)}\) reported emission rates from paper plates and cups in desiccator tests; average emission rates for three different products were 260 to 680 \(\mu g/m^2/day\). These rates were comparable to those from permanent-press fabrics and insulation materials, but were a small fraction (ca. 1-2 percent) of those from wood products. The only other direct emission measurements from paper products found in this study were from wallpaper, as discussed at the end of this section.

The absence of recent HCHO emission data for paper products is probably due to the adoption of "neutral cure" polyamide coatings to impart wet strength, as a replacement for the U-F resins. The polyamide resins contain no formaldehyde. Discussions with representatives of the paper industry and with resin producers\(^{(34-36)}\) disclosed that virtually all consumer paper products now use the polyamide resins. Even common products such as grocery bags or cereal boxes now are made with polyamide resins. M-F resins may be used in some specific products for wet strength, but such products occupy a very small share of the market, and in any case M-F resins are likely to release far less HCHO than do U-F resins. In our information search, the industry sources contacted had trouble identifying any consumer paper products still made with U-F resins, and those that were identified were not products likely to be
found in a home.\textsuperscript{(34-36)} These findings suggest that paper products are no longer significant sources of HCHO to indoor residential air. Furthermore, the residential loading rates of paper products are likely to be very low relative to those of other products.

One possible exception to these conclusions is paper wall coverings. Recent measurements by European investigators\textsuperscript{(37,38)} indicate that small, short-term emission of HCHO may occur from paper-based (as opposed to vinyl, textile or acrylic) wallpaper. It is not clear whether these results apply to wallpaper sold only in Europe, or what the actual source of HCHO is. No comparable U.S. study results were found. The observed emissions decay rapidly, reaching negligible levels in only a few days.\textsuperscript{(37)} The latter finding indicates that exposure is likely to be significant only during and shortly after application of the wallpaper. As a result, the product loading rate of interest is that for the area in which the wallpaper is applied. Assuming all walls of a room are freshly wallpapered, the loading rate would be approximately 0.75-1.5 m\textsuperscript{2}/m\textsuperscript{3} (0.23 to 0.46 ft\textsuperscript{2}/ft\textsuperscript{3}), depending on the room size.

\textbf{3.6 Laminate Products}

In recent work Battelle has evaluated the release of formaldehyde from decorative laminate used (e.g.) for kitchen countertops, table tops, and occasionally for cabinet facings. Those laminates are made with paper layers using P-F and/or M-F resins, and are formed under high pressures and temperatures to promote curing of the resins. Those curing conditions, and the use of relatively low-emitting P-F and M-F resins, minimize HCHO emissions from the finished laminate. Several special purpose laminate varieties exist, with advantages in fire resistance, electrical resistance, or surface durability. However, for this study general purpose grades for countertops and cabinets are of interest.

General purpose laminate is produced in thicknesses of 20-50 mil (i.e., 0.020-0.05 in.) for countertops, and 20 mil for cabinet liners.\textsuperscript{(39)} The Battelle tests show a relatively low emission rate from new standard grade material of up to about 120 \( \mu \)g/m\textsuperscript{2}/day, comparable to the emissions from insulation products, or from some
treated fabrics. We know of no other tests of laminate materials for HCHO emission. In fact, such products were not mentioned in the HCHO studies we surveyed, including an EPA indoor air quality database.\textsuperscript{(40)} The laminate products are not likely to be major sources of HCHO indoors, but the complete absence of any previous emission data indicates that they should be considered in the present study. Particleboard and MDF covered with decorative laminate are common components of furniture and cabinets. It is planned that samples of both the decorative laminates and laminate-coated wood products will be tested in this study.

Decorative laminates are one of a few product categories for which the whole-house loading rate may not completely describe the potential for exposure. In the case of decorative laminates, the reason for this is that laminate use is often concentrated in the kitchen, and therefore any emissions could be concentrated there as well. In the kitchen of a single family home where laminate is used for cabinets as well as countertops, a total of 864 square feet of laminate would typically be present.\textsuperscript{(11,41)} Assuming a 2,000 square foot home,\textsuperscript{(1)} a maximum total loading of 0.18 m$^2$/m$^3$ (0.054 ft$^2$/ft$^3$) results. However, the loading in the kitchen area would be much higher: assuming a 200 square foot kitchen, the loading would be 1.8 m$^2$/m$^3$ (0.54 ft$^2$/ft$^3$). In a 1,000 square foot apartment or mobile home, with a 150 square foot kitchen, the decorative laminate loadings are estimated to be 0.26 m$^2$/m$^3$ (0.081 ft$^2$/ft$^3$) in the home, and 1.8 m$^2$/m$^3$ (0.54 ft$^2$/ft$^3$) in the kitchen.\textsuperscript{(41)} The latter values are based on a total laminate area of 645 square feet.

3.7 Adhesives

This category could potentially include a variety of adhesives, caulks, and sealants. Despite the potentially varied products in this category, and the listing of such products as potential HCHO sources,\textsuperscript{(40)} no useful HCHO emission rate data were found in this survey. The absence of HCHO data may be due largely to changes in adhesive formulations since the presence of formaldehyde indoors became an issue. For example, discussions with the Adhesive and Sealant Council indicate that formaldehyde has very rarely been used in adhesive products for the last 10-15 years.
Recent CPSC guidebooks do not indicate adhesives, other than as used in pressed wood products, to be important indoor HCHO sources.\(^{42,43}\) Some qualitative results from European products suggest water-based adhesives used for textile wallpaper as a significant HCHO source,\(^{44}\) but the applicability of those results to this study is uncertain. Wallpaper adhesives are included in this study by virtue of testing wallpaper itself, under the category of Paper Products.

### 3.8 Cosmetics

Although not suggested as a possible source of HCHO in the EPA database,\(^{40}\) and not among the variety of products tested for the CPSC,\(^{16-18}\) certain cosmetics products may be significant sources of HCHO indoors. The products of likely importance are nail polishes and nail hardeners, which have a substantial HCHO content. Battelle staff have limited experience testing for HCHO from nail polish during application. However, that effort indicated low HCHO emissions, and did not provide a quantitative emission rate measurement. CARB staff have recommended that nail hardeners, rather than polishes, may be the most important cosmetics product in terms of HCHO release. No published measurements of HCHO emission from cosmetics were found in the present study. Contact was made with the Cosmetics, Toiletry, and Fragrance Association, but no information of use to this study was received.

The absence of quantitative emission data might suggest that cosmetic products have not been tested because they are not significant sources of HCHO. In addition, the loading rate of these products within a home will be very small. Only small quantities of these products are likely to be present in a home, and the products are likely to be sealed tightly except during occasional use. However, the means of use of these products may make them important sources of HCHO exposure. Nail polishes/hardeners are unique as the one product category applied to the human body. These nail care products are applied wet, in close proximity to the user, so that exposure may be exaggerated during the infrequent periods of use. In contrast to the product categories that release emissions slowly over an extended time period, nail care
products resemble paints and other coatings in producing elevated emissions that change rapidly over a short period of time. The potential for infrequent but acute exposure to the user suggests that these products should be included for testing in this study. Furthermore, it is probably inappropriate to estimate the loading rate of cosmetic products relative to the entire home volume. Such products are generally applied in a single room, and even in a small area such as a bathroom. This factor tends to increase the potential for HCHO exposure, even though the area-to-volume loading rate of the product will be very small.

3.9 Paints and Coatings

The general category of "wet" consumer products, i.e., paints, coatings, and varnishes, has received considerable attention as a source of volatile organic compounds to both indoor and outdoor air. However, relatively little attention has been devoted specifically to formaldehyde emission from such products. Statements identifying paints and coatings as HCHO sources were encountered often in this information survey\(^{(33,40,42,43)}\) with little quantitative supporting information. The earlier product surveys conducted for the CPSC\(^{(16,18)}\) did not include paints and coatings. The review by Otson and Fellin\(^{(45)}\) suggested latex paint as a source of HCHO; release of formaldehyde for an extended period after application of an unidentified floor finish was also noted. Quantitative emission data are rare, however. A rate of 18 \(\mu g/m^2/\)hour from an acrylic wall paint 14 days after application has been reported.\(^{(46)}\) Emissions from that paint dropped nearly to zero within 28 days after application. No emission rate data were given for freshly applied paint.\(^{(46)}\)

Survey information compiled for the U.S. EPA has indicated that polyvinyl acetate (PVA) latex paints are most likely to emit formaldehyde and other aldehydes.\(^{(47)}\) PVA latex paints are relatively inexpensive and consequently are widely used. Such products are emphasized in the product selection for this category. Unspecified floor cleaning products obtained in France have been reported to release HCHO in substantial quantities,\(^{(44)}\) but the qualitative information given provides no guidance for this study.
In addition to paints, so-called "acid-cured" finishes have been recommended as potential short-term HCHO sources.\textsuperscript{(33,48-50)} These finishes are primarily used in manufacturing facilities where they are spray-applied to finished cabinets or furniture. Acid-cured finishes provide a thin (=0.003 in.), fine, yet very scratch-resistant finish, and so are widely used even on top-of-the-line products.\textsuperscript{(50)} Limited chamber testing of factory-applied acid-cured finishes showed substantial HCHO emissions, with emissions decaying to about 10% of initial values in 3-4 months.\textsuperscript{(49)} Thus HCHO emissions from new cabinets or furniture may include a substantial contribution from the finish coating. These finishes are a two-component product, consisting of a coating and a catalyst that must be mixed. As a result, they are not used directly by consumers. However, such coatings may be applied to wood flooring in homes by commercial contractors.\textsuperscript{(50)} The product used in such cases may be the floor finish alluded to by Otson and Fellin.\textsuperscript{(45)} The few chamber tests of this product showed elevated HCHO emissions, which decayed to 10% of initial values in about 6 months.\textsuperscript{(49)} The HCHO emission rate from acid-cured floor finishes applied in the home is undoubtedly greater than that from finishes commercially applied to products which later end up in the home. However, the latter is certainly the more widespread means of introduction of acid-cured finishes into the home. Acid-cured finishes appear to be a potential indoor HCHO source which has not received significant attention. As a result, both the commercially applied and in-home use of such finishes are included in this product selection process.

Paints and coatings applied indoors are similar to cosmetics (Section 3.8) and wallpaper (Section 3.5) in that exposure in a portion of the home during application may be more important than the overall loading rate of coated surfaces within the home. If the product in question is an interior wall paint, and all walls are painted, then the likely in-home loading rate should be similar to the in-room loading rate, at approximately 0.75-1.5 m\textsuperscript{2}/m\textsuperscript{3} (0.23 to 0.46 ft\textsuperscript{2}/ft\textsuperscript{3}). The loading rate expected of a floor coating or cleaning product is about 0.41 m\textsuperscript{2}/m\textsuperscript{3} (0.13 ft\textsuperscript{2}/ft\textsuperscript{3}).
3.10. HCHO Product Summary

Table 4 summarizes information on each of the product categories reviewed in Sections 3.1 to 3.9. Shown in Table 4 are the range of reported values for the emission rate, the likely range of in-home loading rate, amount produced, and the intensity of exposure that may result from each product. For some products, separate loading rates could be estimated in conventional, mobile, and multi-family residences. Note that the summary loading rates shown in Table 4 are the sum of loadings in various uses of the product, as applicable. For example, the particleboard loadings include uses in flooring, cabinets, trim, and furniture. For some products, the product loading rate in the room where the product is concentrated or applied is also shown. Most of the entries shown in Table 4 are summaries of the data reviewed in Sections 3.1 to 3.9. However, for some product categories some entries had to be estimated because of a lack of data. The "intensity of exposure" is estimated only as low, medium, or high, depending on the way in which the product is used.

The initial intent of this product selection process was to achieve a quantitative ranking of each product category on the key characteristics shown in Table 4. The rankings on individual characteristics were then to be rolled up into an overall ranking, on the basis of which the numbers of samples to be tested would be defined. However, the product selection which has been achieved is only semiquantitative, for three reasons. First, quantitative data are not available for all key characteristics for all products. Second, considerable variation exists within the data available for any single category, because of differences in the methods used and the products considered, and due to changes in products and product uses over time. Third, not all the product characteristics are amenable to quantitative assessment. This is particularly true for the "intensity of exposure" factor, which is intended to address aspects of product use that enhance or limit user exposure to HCHO. Such factors are impossible to fully quantify based on current information. As a result, the product selection process is best described as an informed subjective judgment, based on the available quantitative data.

The emission rate data shown in Table 4 are those stated in Sections 3.1-3.9. The same is true for the loading rate data for wood products and laminates. However,
<table>
<thead>
<tr>
<th>Product Type</th>
<th>HCHO Emission Rate (µg/m²/d)</th>
<th>Total Loading* (m²/m²)</th>
<th>Quantity Used/Produced (10⁶ ft²)</th>
<th>Estimated Exposure Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CSF</td>
<td>MH</td>
<td>MF</td>
</tr>
<tr>
<td>Wood Products:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-F</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particleboard</td>
<td>460-168,000</td>
<td>0.51-0.94</td>
<td>0.73-0.93</td>
<td>0.54-0.69</td>
</tr>
<tr>
<td>Hardwood Plywood</td>
<td>140-68,000</td>
<td>0.53-0.77</td>
<td>0.46-1.3</td>
<td>~0.5</td>
</tr>
<tr>
<td>Medium Density Fiberboard</td>
<td>9,300-55,000</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardboard</td>
<td>?</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-F</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oriented Strand Board</td>
<td>&lt; 2,000</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Softwood Plywood</td>
<td>&lt; 2,000</td>
<td>0.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exterior Particleboard</td>
<td>&lt; 2,000</td>
<td>~0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other Products</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laminates</td>
<td>120</td>
<td>0.18</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>Fabrics</td>
<td>15-750</td>
<td>~0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insulation</td>
<td>52-3,000</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coatings/Paints</td>
<td>&lt; 500</td>
<td>0.75-1.5</td>
<td>0.75-1.5</td>
<td></td>
</tr>
<tr>
<td>Cosmetics</td>
<td>?</td>
<td>&lt; 0.001</td>
<td></td>
<td>&lt; 0.005</td>
</tr>
<tr>
<td>Paper Products</td>
<td>260-680</td>
<td>0.75-1.5</td>
<td>0.75-1.5</td>
<td></td>
</tr>
<tr>
<td>Carpets</td>
<td>10-1,500</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adhesives</td>
<td>?</td>
<td>&lt; 0.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Total loading in the home based on summation of separate loadings in various uses of the product (e.g., flooring, furniture, etc.). CSF = conventional single-family; MH = mobile home; MF = multi-family; I-R = in-room where use or application is concentrated.
(b) Estimate based on sum of draperies, linens, and new clothes.
(c) Estimate based on fiberglass ceiling tiles on 1/4 of ceiling area in a 2,000 ft² home.
(d) Estimate based on coverage of all interior walls; loading of a floor coating would be about 0.41 m²/m².
(e) Estimate based on likely use of the product.
(f) Estimate for wallpaper; loading rates of other paper products are likely to be < 0.05.
(g) Recent information suggests formaldehyde is not present in these product types as used in homes.

? No data obtained.
for the other product types, loading rates were estimated, as indicated in the footnotes to Table 4. These estimates are based on the likely use of the products, and are probably upper limits to the actual loading rates. For example, the loading rate for coatings assumes that HCHO-emitting coatings are used on all internal wall surfaces of the home. Estimated loading rates are listed only for conventional single-family homes in Table 4; the corresponding loadings in mobile and multi-family homes would probably be similar. Production data are shown in Table 4 only for some wood products. Although such data presumably are available for all the products, this information was not judged sufficiently important to pursue it for all products.

The estimated exposure intensity values in Table 4 are stated as High, Medium, or Low, depending on the proximity of the user and the duration and intensity of the exposure. Products rated Low are those which are relatively isolated from the indoor space and likely to release HCHO slowly and over a long time period. P-F products used as subflooring are a prime example, separated as they are from the indoor space by underlayment, carpeting, or other floor coverings. Products rated Medium in exposure intensity are those that emit directly into the indoor space, at moderate levels, and over a relatively long time period. U-F products used in cabinets, furniture, and trim are a good example of such products. Those products rated High in exposure intensity are those that may produce elevated HCHO exposure in relatively brief periods of use. Coatings and cosmetics fall in this category, as wet products for which the user is in close proximity to the product during application and curing. These products may cause relatively elevated HCHO levels near the point of application, whether or not they contribute substantially to HCHO levels throughout the home. No exposure intensity estimates are shown in Table 4 for carpets or adhesives, two product types which are not currently considered to be significant in-home formaldehyde sources.

3.11 HCHO Product Selection

The information summarized in Table 4 has been used to define the number of products of various types to be tested in this study, with the aim of selecting 50 or
more total samples for testing. The goal of the selection process is to emphasize the
most significant indoor HCHO sources, based on the collected information, but to also
include samples of the minor source types as well. The product categories, the
identities of specific sample types, and the numbers of each to be tested, are shown in
Table 5. At least two different samples will be tested from all product types, with the
exception of carpets and adhesives. Current information indicates that those product
categories are not significant HCHO sources, so no testing will be done on such
products. The following are descriptions of the reasoning used in selecting the specific
products listed in Table 5.

The emphasis on selecting U-F wood products over P-F products is a direct result
of the greater reported emission rates of the U-F products, and also of the higher
loading rates of some U-F products. Within the U-F category the number of samples
from each product type was weighted by the amount of material produced and by the
loading rates of the various product types (Table 4). For example, in the U-F category,
the largest number of samples was selected from the particleboard group, because of
the very large production of this type of product. Equal numbers of samples of MDF
and hardwood plywood are planned. Although hardwood plywood is produced in
somewhat larger quantities, and may have a somewhat higher in-home loading rate,
MDF is reported to be the wood product that is highest in HCHO emissions. These
counterbalancing factors led to equal emphasis in sample selection. The low emission
rate and low loading of hardboard products resulted in minimal selection of such
products for testing. Within the P-F group, the loading rates in Table 4 and the
possibly increasing use of exterior particleboard in flooring\(^{(43)}\) led to selection of one
sample each of softwood plywood, OSB, and exterior particleboard.

The HCHO emission rates of all other product categories were reported to be
much less than those of U-F wood products, and in most cases the loading rates are
smaller as well. As a result, relatively small numbers of samples (i.e., 3-4) were
selected from each category.

Within each category and product type, specific sample products were identified,
as shown in Table 5. The identification of these products and the number of samples
selected were based on the information described in Sections 3.1 to 3.10. For wood
<table>
<thead>
<tr>
<th>Category/Type</th>
<th>Sample Identity</th>
<th>Number of Samples to be Tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-F Wood Products:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particleboard</td>
<td>5/8 in. Floor Underlayment</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>5/8 in. Mobile Home Decking</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3/4 in. Industrial Particleboard</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>5/8 in. Industrial Particleboard</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3/4 in. Industrial Particleboard, with melamine laminate both sides - domestically produced</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3/4 in. Industrial Particleboard, with melamine laminate both sides - imported</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>5/8 in. Industrial Particleboard, with 2-5 mil vinyl coating both sides</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>5/8 in. Industrial Particleboard, with e'-cured-acrylic gloss finish both sides</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Interior Wood Door with Industrial Particleboard core</td>
<td>1</td>
</tr>
<tr>
<td>Total Particleboard</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Medium Density Fiberboard</td>
<td>3/4 in. MDF-unlaminated</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3/4 in. MDF, with UV-cured filler both sides</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3/4 in. MDF, with melamine laminate both sides</td>
<td>2</td>
</tr>
<tr>
<td>Total MDF</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Hardwood Plywood</td>
<td>3/4 in. Stock Plywood</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1/4 in. Prefinished Wall Panelling</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1/4 in. Stock Plywood</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1/2 in. Stock Plywood</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1/2 in. Hardwood Veneer Plywood</td>
<td>1</td>
</tr>
<tr>
<td>Total Hardwood Plywood</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Category/Type</td>
<td>Sample Identity</td>
<td>Number of Samples to be Tested</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------------------------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td><strong>U-F Wood Products:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Continued)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardboard</td>
<td>1/4 in. Hardboard Sheet</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1/4 in. Perforated Hardboard, i.e., &quot;pegboard&quot;</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td><strong>Total Hardboard</strong></td>
<td><strong>2</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Total U-F Products</strong></td>
<td><strong>32</strong></td>
</tr>
<tr>
<td><strong>P-F Wood Products:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oriented Strand Board</td>
<td>3/4 in. OSB</td>
<td>1</td>
</tr>
<tr>
<td>Softwood Plywood</td>
<td>3/4 in. Softwood Plywood</td>
<td>1</td>
</tr>
<tr>
<td>Exterior Particleboard</td>
<td>3/4 in. Exterior Particleboard</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td><strong>Total P-F Products</strong></td>
<td><strong>3</strong></td>
</tr>
<tr>
<td><strong>Decorative Laminates:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 mil General Purpose Laminate</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>50 mil General Purpose Laminate</td>
<td>1(^a)</td>
</tr>
<tr>
<td></td>
<td>20 mil Cabinet-liner Type Laminate, for interior</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>cabinet surfaces</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Total Laminates</strong></td>
<td><strong>3</strong></td>
</tr>
<tr>
<td><strong>Fabrics:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Permanent Press Dress Shirts</td>
<td>2(^b)</td>
</tr>
<tr>
<td></td>
<td>Permanent Press Bed Sheets</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Permanent Press Drapery Fabric</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td><strong>Total Fabrics</strong></td>
<td><strong>4</strong></td>
</tr>
<tr>
<td><strong>Insulation:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fiberglass ceiling panels, 3/4 in. thickness</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Fiberglass roll insulation, unfaced, R-19 rating</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td><strong>Total Insulation</strong></td>
<td><strong>3</strong></td>
</tr>
<tr>
<td>Category/Type</td>
<td>Sample Identity</td>
<td>Number of Samples to be Tested</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-------------------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Coatings/Paints:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinylacetate Interior Latex Paint</td>
<td>2*</td>
<td></td>
</tr>
<tr>
<td>Commercially Applied Acid-Cured Finish</td>
<td>1*</td>
<td></td>
</tr>
<tr>
<td>Acid-Cured Floor Finish</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total Paints and Coatings</td>
<td>4</td>
</tr>
<tr>
<td>Cosmetics:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nail Hardeners</td>
<td>2*</td>
<td></td>
</tr>
<tr>
<td>Nail Polish</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total Cosmetics</td>
<td>3</td>
</tr>
<tr>
<td>Paper Products:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paper-based Wall Coverings</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Paper Towels</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Paper Grocery Bags</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total Paper</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Total Samples, All Categories</td>
<td>56</td>
</tr>
</tbody>
</table>

(a) One duplicate sample will be obtained of this product, and subjected to testing for HCHO emission, to assess repeatability of the test procedures.

(b) Clothing samples will be tested both before and after washing.

(c) This coating will be tested by conducting tests on uncoated cabinet doors, and on cabinet doors coated with acid-cured finish at the factory; i.e., two sets of emission tests will be done.
products, the production data and end uses of various product types were the key factors considered. For example, floor underlayment, mobile home decking, and door cores comprise small portions of the total particleboard production, so relatively few samples, of the most common thickness, are planned for those products. Most particleboard production is industrial particleboard, and much of that is coated or laminated for use in end products such as furniture and shelving found in the home. As a result, the industrial particleboard samples predominate, and are spread among a variety of common products, including vinyl- and laminate-coated boards. Also listed is one sample of particleboard coated with electron-beam-cured acrylic, a hard, glossy finish often used for applications such as stereo speaker cabinets and furniture. All of the various coated particleboard products – whether vinyl, laminate, or acrylic coated – are included in order to represent the materials that actually are present in residences, as opposed to the raw particleboard base material. The identification of these samples included review of product information provided by the National Particleboard Association.\(^2,3\) The samples identified are in the most common sizes. In obtaining particleboard products for testing, an effort will be made to obtain the same particleboard in both coated and uncoated forms. Such samples would allow a direct comparison of the effect of vinyl, laminate, or acrylic coatings on particleboard HCHO emissions. Discussions with a large distributor of U-F wood products in California\(^{51}\) disclosed that laminate-coated particleboard was one product for which a domestic/imported comparison could also be done. The sample selection shown in Table 5 includes such a comparison.

Sample identification for MDF, hardwood plywood, hardboard, and P-F products followed similar lines. The most common sample thicknesses and uses were chosen. The melamine laminate coated MDF is a common form in which MDF actually exists in residences. In the same way as for the particleboard products described above, an effort will be made to obtain the same MDF both with and without the laminate coating, to assess the effect of the coating on HCHO emissions. The UV-cured filler MDF is a common product to which liquid and printed coatings are applied. As such, this product also is a common form in which MDF occurs in homes. In the hardwood plywood category, a range of common stock plywood sizes are selected, reflecting the
wide usage of that product. Only one sample of hardwood plywood wall panelling is
planned, due to the diminishing use of that product. Instead, stock plywood is the
dominant plywood product selected. An effort will be made to obtain the same plywood
material with and without a hardwood veneer, to assess the effect of the veneer on
emissions.

The decorative laminates to be tested cover the range of thicknesses of general
purpose and cabinet-liner types. The testing of laminate-coated particleboard and MDF
will augment the tests conducted on laminates alone.

Fabric samples to be tested include clothing, bed sheets, and draperies. Reported
HCHO emission rates for clothing were the highest among fabric samples tested
previously. Clothing samples will be tested both before and after washing.

Samples of insulation products will include both ceiling tiles and roll insulation
such as might be found in an attic. Paints to be tested include both PVA latex and
acid-cured finishes, because the very limited information available suggests those
products as significant HCHO sources. Acid-cured finishes will include both the floor
finish applied in the home, and the factory-applied finish on kitchen cabinet doors. The
latter will be tested by a dual set of emission measurements: both uncoated doors and
coated doors will be obtained from a cabinet maker supplying the California market.\(^{(52)}\)

Samples of cosmetics will consist of nail hardeners and nail polish. The latter is
thought to produce lower HCHO emission than nail hardeners, but may be used by many
consumers who do not use the nail hardeners. These products may be specially labelled
if they contain relatively large amounts of formaldehyde. Any such labelling will be used
as a guide in obtaining the products.

Paper products tested will consist of samples of paper-based wall coverings, plus
one sample each of paper towels and grocery bags. The latter products are no longer
considered to be likely sources of HCHO, but samples of common products will be tested
to assess that view.

Table 5 shows that a total of 56 samples are planned for testing. Of that total, 48
are solid materials, and 8 are "wet" products, including 2 samples of wallpaper, that will
be tested during application. However, one of the solid material tests is on an
acid-cured finish commercially applied by a manufacturer, i.e., a "wet" product after drying. In addition, the 2 samples of clothing will each be tested twice, i.e., before and after washing. The commercially-applied acid-cured finish also will require 2 test runs, as noted above. Furthermore, a total of 10 duplicate samples are planned, as indicated in Table 5. For selected products duplicate test samples will be obtained and subjected to separate HCHO emission tests, as a measure of the repeatability of the test procedures. The duplicate sampling/testing runs are apportioned to 8 solid and 2 wet samples, consistent with the relative total number of solid and wet samples. The duplicate sampling and testing will be done on samples that Battelle considers particularly important as potential HCHO sources, or representative of key product types.

4. TDI PRODUCTS

The survey for information on TDI-containing products included direct contacts with representatives of industries making or using TDI, discussions with scientists involved in the very limited previous investigations of TDI emissions, contacts with retailers of polyurethane products, and reviews of literature and published reports. Although considerable information exists on the industrial uses, chemistry, and even the atmospheric fate of TDI, virtually no information was found on any release of TDI to air from consumer products. Contacts with members of the International Isocyanates Institute\(^{(53)}\) and representatives of the Society for the Plastics Industry\(^{(54)}\) did not produce useful information for this product selection.

The types of products manufactured with TDI are quite well known. Production of flexible polyurethane foam for furniture cushions and carpet padding is by far the largest single use of TDI, and these products are probably the most prevalent TDI-containing materials in a home. Hodgson and Wooley\(^{(55)}\) identified several potential product categories for TDI, including polyurethane foams; elastomers used for fabric coating; varnishes and paints; cement sealers; and adhesives and mastic sealants used in construction of homes. The latter sealants were stated to contain up to 7.6 percent TDI by weight.\(^{(55)}\) Those researchers recommended inclusion of polyurethane carpet pads,
furniture cushions, varnishes, and caulks in a study to screen for possible TDI emissions.

Very little information exists on TDI emission from consumer products. Recent studies of organic emissions from carpets\textsuperscript{30,31} found no detectable TDI emissions from urethane-backed carpets. However, that was a screening level test only, and the CPSC report indicates that further evaluation of TDI release is being conducted as part of a follow-on study of carpet padding.\textsuperscript{30} It was necessary to complete this product selection process before completion of that CPSC report on carpet padding. However the results of that study will be factored into this work when the report becomes available. Screening-level tests for TDI from a variety of coatings and liquid products, conducted as part of an analytical method development effort, also disclosed no indication of TDI emissions.\textsuperscript{56}

Interesting results have been obtained in air sampling at polyurethane foam production facilities.\textsuperscript{57} Those results show that TDI emissions from the finishing end of the production line are almost entirely in the form of the 2,6-TDI isomer, even though the starting isomeric mixture was 80 percent 2,4-. 20 percent 2,6-TDI. The reason for this is the greater reactivity of the 2,4-isomer, and its consequent greater consumption in the urethane production process.\textsuperscript{57} This finding suggests that TDI emissions from consumer products may also be heavily weighted toward the 2,6-isomer. This suggestion has two implications for the present study. First, any TDI measurement method used for the screening tests must be at least as sensitive to the 2,6-isomer as to the 2,4-isomer. Lower sensitivity to the 2,6-isomer might handicap the screening tests. Second, an analytical method that separates quantitates the two isomers is preferable to one that does not. Determination of the isomeric ratio of any emitted TDI could confirm the workplace results,\textsuperscript{57} and may be important for estimating the toxic effects of any emissions. Toxicological tests have generally been assessed using 2,4-TDI or the standard 80/20 mixture, but there may be differences in the toxic potency of the two isomers.\textsuperscript{57}

Based on the limited information available, a product selection was completed for an initial emission screening of TDI products. This selection could not be made as quantitative as that for the HCHO products, but product selection was weighted based
on the information available. Table 6 shows the information at hand on TDI products, in a format analogous to that of Table 4 for HCHO products. That table shows the results of the TDI product selection, indicating the category of TDI product, the identity and number of product samples to be screened from that category, and the rationale or qualitative weighting given each category. Table 6 also highlights the absence of information on TDI emission rates. A total of 49 samples are planned for TDI screening at this time. The categories of carpet padding, foam cushions, and polyurethane coatings are weighted more heavily in product selection, because these are the primary polyurethane products found in homes. The category of caulks/sealants is weighted somewhat lower, because the primary uses of such products are likely to be outside the living space of a home.

The relative numbers of samples planned for each sub-type of TDI product within each category are based on Battelle's current estimation of the use of these products, the likely loadings in the home, and the potential for exposure. For example, the distribution of carpet padding samples is based on contacts with retailers who indicated the most common thicknesses, and the relatively small market share of foam-backed carpet. More samples of wood finishes and varnishes are planned than of spray paints, because of the likely greater indoor use of the former products. Similarly, concrete sealants will be screened in larger numbers than will construction caulking materials, because the former offer a greater potential for exposure and may be used repeatedly over the life of a home (e.g., in a garage), rather than merely at the time of construction. The smallest number of samples to be screened is from the category of polyurethane coated fabrics. Such products are thin, fully cured coatings that are unlikely to have substantial emissions for long after manufacture. Further information on all the indicated product categories will be obtained throughout the process of obtaining TDI products, and the product selection outlined in Table 6 will be modified as necessary in light of any new information. Battelle will use a subcontractor to actually obtain the products in California; a description of that subcontractor's role in defining and carrying out product selection is given in Section 5.

Some of the planned TDI products are typically used or found preferentially in some part of the home. Others may produce product loading rates or exposure during
<table>
<thead>
<tr>
<th>Product Type</th>
<th>TDI Emission Rate</th>
<th>Loading (m²/m³)*</th>
<th>Estimated Exposure Intensity</th>
<th>Rationale/Weighting</th>
<th>Number of Samples to be Screened</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carpet Padding:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foam-backed carpet</td>
<td>?</td>
<td>0.3</td>
<td>Low</td>
<td>Large fraction of polyurethane production; widespread use and relatively high loading in homes; under investigation in CPSC study.</td>
<td>2</td>
</tr>
<tr>
<td>Padding 3/8 in.</td>
<td>?</td>
<td>0.3</td>
<td>Low</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Padding 1/2 in.</td>
<td>?</td>
<td>0.3</td>
<td>Low</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Padding 9/16 in.</td>
<td>?</td>
<td>0.3</td>
<td>Low</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td><strong>Foam Cushions:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Furniture cushions</td>
<td>?</td>
<td>0.05</td>
<td>Medium</td>
<td>Large fraction of polyurethane production; widespread use and relatively high loading in homes.</td>
<td>6</td>
</tr>
<tr>
<td>Foam mattresses</td>
<td>?</td>
<td>&lt;0.05</td>
<td>0.1</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Sheet foam material</td>
<td>?</td>
<td>&lt;0.05</td>
<td>Medium</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td><strong>Polyurethane Coatings:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood finishes, Varnishes</td>
<td>?</td>
<td>0.1</td>
<td>0.4</td>
<td>High clearance potential for high emissions during application; reasonably widespread use and moderate loading in homes.</td>
<td>8</td>
</tr>
<tr>
<td>Spray polyurethane paints</td>
<td>?</td>
<td>&lt;0.05</td>
<td>0.1</td>
<td>High clearance potential for high emissions during application; reasonably widespread use and moderate loading in homes.</td>
<td>4</td>
</tr>
<tr>
<td><strong>Polyurethane Coated Fabrics:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waterproofed Fabrics</td>
<td>?</td>
<td>&lt;0.05</td>
<td>Low</td>
<td>Emissions likely to decay rapidly; probably minimal loading in homes.</td>
<td>5</td>
</tr>
</tbody>
</table>

Subtotal 12

Subtotal 12

Subtotal 12

Subtotal 12

Subtotal 5
TABLE 6. (Continued)

<table>
<thead>
<tr>
<th>Product Type</th>
<th>TDI Emission Rate</th>
<th>Loading (m³/m³)ᵃ</th>
<th>Estimated Exposure Intensity</th>
<th>Rationale/Weighting</th>
<th>Number of Samples to be Screened</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caulks and Sealants:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concrete sealer</td>
<td>?</td>
<td>&lt;0.05</td>
<td>0.3</td>
<td>High</td>
<td>5</td>
</tr>
<tr>
<td>Mastic construction sealants</td>
<td>?</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>Loading in home likely to be small; use may be predominantly outside the living space; potential for high emissions during application, in the case of concrete sealants.</td>
<td>3</td>
</tr>
<tr>
<td>Subtotal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>49</td>
</tr>
</tbody>
</table>

(a) All loading rates shown are estimates based on likely use of the product.
(b) I-R refers to in-room loading rate, for a product where loading or application may differ substantially from whole-house loading rate.
? No information available.
application that are not typical of the entire home. For those products, Table 6 includes both a whole-house and an in-room (I-R) loading rate, the latter pertinent to the area where the product is concentrated or applied. All the TDI products listed with both loading rates in Table 6 are wet products, except for foam mattresses, for which the I-R loading refers to the product loading in a bedroom. Application of a coating to the entire floor of a room may produce an I-R loading of up to 0.4 m²/m³ (Table 6). Note that in general the whole-home loading rates of the TDI products are relatively low, except for carpet padding, which may be widely used in a home.

The exposure intensity levels in Table 6 reflect primarily the proximity of residents to any emissions. The wet TDI products have the potential to produce relatively higher TDI emissions.

5. PRODUCT ACQUISITION

The products identified in section 3.11 for HCHO emission testing and in section 4 for TDI emission screening will be purchased in the California marketplace by a Battelle subcontractor, KKO Laboratories (KKO). The purpose of this section is to describe the planned role of the subcontractor, and the ways that samples will be obtained for this study.

Battelle's selection of test samples, set forth in Tables 5 and 6, is as specific as the available information will allow. To some extent, Battelle will simply direct KKO to purchase the specified items. However, for some samples only incomplete information exists, and for all samples proper choice of the source of purchased samples is important. In addition, documentation of the origin and identity of all samples is needed. As a result, acquisition of test samples will rely on collaboration between Battelle staff and KKO. Communication between the two organizations has been established long before the specification of test samples, to assure that such collaboration takes place.

Battelle will provide KKO with a list of sample specifications equivalent to Tables 5 and 6, and with further information such as the quantity or size of test sample needed. The size of samples needed is defined by the product loading rate in the test.
chambers. Loading rates for all products to be tested will be specified in written chamber test procedures, prepared before acquisition of any samples. The need for duplicate samples will be specified for certain products, as well. To some extent, Battelle will also specify sources for purchase of specific test items, as described below. However, there are likely to be some identifying characteristics that cannot be defined until product acquisition is actually in progress. An example could be the most commonly used brand of some product of interest. In such cases, KKO's role will be to make the necessary inquiries to obtain the most widely used or representative products for testing. The means that KKO uses to make those inquiries may include direct questioning of retailers, wholesalers, or users of the products in question; review of Material Safety Data Sheets on hand at retail outlets; and calls to manufacturers. Battelle will assist as much as possible in these inquiries, but the experience and judgment of KKO staff will be particularly valuable in this effort.

Samples of products for testing will be obtained from more than one location in California, in areas of active construction and expansion of homes and apartments. KKO staff have recommended several growing communities in the San Francisco Bay area as likely source regions, and CARB staff have suggested the Sacramento area as another actively growing area. The Los Angeles basin area is a very large market region, and will also be included. It is planned that KKO staff will make sample acquisition trips of a few days to different parts of the state, so that comparable samples of specific types are obtained from different outlets in the different areas.

Products will be obtained from a mixture of sources, intended to represent the avenues by which the products would realistically end up in residences. Retail outlets that move substantial amounts of material will be emphasized. For some products, industry sources will be used. At Battelle's request, the particleboard industry has identified Southwest Plywood and Lumber Corporation (SPLC), of Rancho Dominguez, California, as a source for a variety of wood products. Contact with SPLC has confirmed their willingness to assist in obtaining samples. One advantage of using SPLC is that a number of wood products may be obtained that would be difficult to find in the retail marketplace, such as particleboard and MDF materials that become components of furniture and cabinets. In fact, the furniture industry is SPLC's primary
customer. Given the large loading of such products in homes, this is an important consideration. SPLC will allow Battelle/KKO to purchase small quantities of material for testing, in contrast to the large volumes ordinarily sold to industrial customers. Another advantage is that SPLC can provide detailed documentation of the nature and source of the products tested, allowing such information as product age to be determined accurately. To the extent possible, wood products will be obtained in both plain and coated forms (i.e., with vinyl, laminate, or "Cortron" coatings), to allow comparisons of HCHO emissions. This information also allows comparison of domestic and imported products (see Table 5), which would be difficult to distinguish otherwise.

The use of an industrial source such as SPLC for test samples could introduce the appearance of bias in sample selection, despite the several advantages of such a source for the project. To address this issue, only a portion of the needed products will be obtained from SPLC; samples of the same products will also be obtained from other sources in other parts of the state, for comparison to those from SPLC. For example, we plan that industrial particleboard, MDF, and U-F plywood of identical thicknesses will be obtained from SPLC and from other outlets. The number of samples to be obtained in different parts of the state will be specified by Battelle in instructions to KKO.

All samples will be purchased by KKO as part of the project. For this purpose, Battelle has set up KKO's subcontract to include an allocation specifically for purchasing samples. That full allocation will be provided to KKO at the start of the sample acquisition process, so that acquisition of samples is not impeded by the cost of purchases. Upon purchasing samples, KKO will document the date, location, and source of the purchase; the product identity and characteristics; any background or history on the product; and any further information on the representativeness of the sample. The latter may include specific inquiries made regarding the product. This documentation will accompany the samples shipped to Battelle, and KKO will retain one copy of the sample documentation and associated shipping information. For purposes of recording the information at the time of purchase, Battelle will provide KKO with prepared blank forms to be filled in.

A-40
REFERENCES


2. 1993 U.S. Annual Shipments & Production, National Particleboard Association, Gaithersburg, Maryland, 6 pp.


28. Personal Communications from Hardy B. Poole, American Textile Manufacturers Institute, October and November 1994.


47. Personal communication from Al Censullo, California Polytechnic, San Luis Obispo, January, 1995.


50. Personal communication from T. Godish, Ball State University, January, 1995.


54. Personal communication from Fran Liechtenberg, SPI, October 1994.


A-45
APPENDIX B

PROTOCOL FOR CHAMBER TESTING OF
FORMALDEHYDE EMISSIONS FROM
INDOOR RESIDENTIAL SOURCES

The document shown in this Appendix was prepared during the course of Research Project 93-315, and served as the basis for a portion of the project. However, the main body of this report should be consulted as the most complete and final presentation of the study activities and results.
PROTOCOL FOR CHAMBER TESTING OF FORMALDEHYDE EMISSIONS FROM INDOOR RESIDENTIAL SOURCES

California Air Resources Board Project 93-315

prepared by
Battelle
505 King Avenue
Columbus, Ohio 43201-2693

Revision Date: June 6, 1995

1. Scope

1.1 This protocol states the procedures to be used for testing of formaldehyde emissions from indoor residential sources in the California Air Resources Board project identified above. Emissions from such sources are determined by measurements of formaldehyde concentration in medium-size chambers under conditions of controlled temperature, humidity, and air flow. The formaldehyde content of chamber air is determined by the 2,4-dinitrophenylhydrazine (DNPH) method (U.S. EPA Compendium Method TO-5). Other analytical procedures may be used if they provide formaldehyde results comparable to those from the DNPH procedure, however, the DNPH method also provides measurement of other carbonyl compounds in the same analysis. Additional compounds to be determined by the DNPH method in this study include acetaldehyde (which is listed in both the 1990 Clean Air Act Amendments list of Hazardous Air Pollutants (HAPs) and in California’s Proposition 65 list of chemicals), and propionaldehyde, methyl ethyl ketone, and methyl iso-butyl ketone (which are all on the HAPs list).

This protocol also employs an additional continuous real-time monitoring method for formaldehyde. This method is used to document that steady state conditions have been achieved in the chamber, and as a backup for the DNPH method. The real-time method is required for performance of this protocol, except under a few specific circumstances in which the product behavior is already sufficiently well known.

1.2 This protocol calls for performance of emission tests at two separate test conditions simultaneously in twin chambers, each maintained at one of the two conditions. This approach offers advantages in efficiency and precision of test performance. However, performance of the tests in a single chamber by sequentially adjusting test conditions may also be suitable, provided that such an approach provides reproducibility of test conditions and test results comparable to those obtained with separate chambers.

1.3 The protocol stated here is designed for testing of "dry" products, i.e., those that do not need an application, spraying, or drying step to simulate normal use. The dry products for which this protocol is intended include wood products such as particleboard, plywood, and fiberboard; decorative laminates; fabrics; insulation materials; and paper products. The chamber conditions and loading rates for testing of these products are specified in this protocol. The general procedure described here may be applied to other products not specifically named, provided the test results are properly documented with the loading rates and test conditions used.
Dry Product Protocol
Revision: June 6, 1995

1.4 A separate test protocol exists for testing of "wet" products in this study. Those products include paints, coatings, and cosmetics.

1.5 Hazards associated with the chemicals and procedures used in this protocol are stated in section 7. However, this protocol does not purport to address all of the potential safety issues resulting from its use. The user of this protocol is responsible for establishing safe operating conditions and procedures.

2. References

2.1 Published documents that are the basis for this protocol are cited by means of Arabic numeral superscripts, and are listed in numerical order at the end of this document.

3. Terminology

3.1 The terms used in this protocol are common in the field of chamber testing. The reader is referred to standard chamber test procedures (e.g., 1,2) for background on the terms used.

4. Significance and Use

4.1 This test protocol is specifically designed for the performance of chamber tests by Battelle for the purposes of the CARB project cited above. The aim of this project is to obtain formaldehyde emission rate data for a wide variety of products used in homes in California. The results of this project are intended to update similar test results obtained a decade or more ago by the Consumer Product Safety Commission.3,4 The test results will allow CARB to inform the public as to what are the most important indoor formaldehyde sources, with the goal of reducing the indoor formaldehyde exposure of the California populace.

4.2 The test protocol uses twin stainless steel and glass chambers of 1.43 m³ volume, for testing at two sets of conditions. The chamber temperature, humidity, air exchange rate, and internal mixing are controlled. Product loading rates, i.e., the exposed surface area of the material tested per unit volume of the chamber, are also specified for the various products. Test samples are held at constant conditions in the chambers for at least 16 hours before the chamber air is sampled for determination of formaldehyde and other aldehydes.

4.3 The two sets of test conditions are representative of typical and high-end indoor conditions, in terms of the temperature and air exchange rates. The intent of this selection is to bracket the emission rates to be expected in homes.

4.4 Although the test procedures are designed to provide emission rates that are realistic relative to those that may occur in a home, caution must be used in extrapolating the test results to any real home or to other test conditions. The test results are primarily intended to allow comparison of different product types.
5. Apparatus

5.1 Test Chambers: Tests are conducted in two chambers located side-by-side in Battelle’s laboratories. Each chamber has a volume of 1.43 m³, and is built of stainless steel and glass. The front face of each chamber is a door of 80 cm x 125 cm dimensions, consisting of a nearly full size glass pane in a steel frame. The doors are self-sealing by means of elastomer seal strips which are minimally exposed to air movement within the chamber once the door is closed. External clamps on the circumference of the doors assure retention of the seal during testing. Steel mesh shelving can be positioned at several vertical locations for support of test samples in the chambers.

5.2 Internal Mixing: A fan is located near the top of each chamber to promote mixing of air within the chamber. These fans are driven by electric motors located outside the chambers. The air movement from the fan is partially obstructed by a baffle so that air flow is not directly at the test samples.

5.3 Clean Air Supply: The air flow into the chambers is provided by an Aadco pure air generation system, which removes water vapor, particulate matter, and gaseous contaminants from outdoor ambient air. The formaldehyde content of the air from this supply is less than 0.1 ppbv (0.12 micrograms per cubic meter, ug/m³), and the total content of other organic contaminants is less than 20 ppbv. The flows of dry and humidified Aadco air into the chambers are controlled by mass flow controllers of 10 to 30 L/min capacity (Tylan or comparable). Those flowmeters are calibrated at regular intervals (independent of this study) by comparison to known flow standards in Battelle’s central Instrument Laboratory. The test chambers operate at a slight positive pressure, i.e., < 0.2 psig, which is monitored by Manohelic gauges. Air leaving the chambers is drawn into a vacuum duct and is exhausted into a laboratory hood and subsequently outdoors.

5.4 Air Sampling Ports: Each chamber is equipped with several ports suitable for sampling. Air sampling is conducted by extending a Teflon sampling tube (6 mm O.D. or similar) to about the midpoint of the chamber, but no closer than 30 cm from any surface of the test sample. Sampling apparatus is located on tables next to the chambers, assuring that sampling lines are as short as possible.

5.5 Air Sampling and Analysis Methods: Determination of formaldehyde and other carbonyl compounds is accomplished using EPA Compendium Method TO-5, which involves impingers containing DPNH in acetonitrile solution. Details of this method can be found in the appropriate EPA document. Additional real-time formaldehyde measurements are made with a monitor developed by Battelle under EPA support. That monitor employs continuous collection and derivatization of formaldehyde, using continuous fluorescence as the final analytical technique. The monitor is located near the test chambers, and samples from either chamber as needed. Details of the operation of this instrument have been published.
Dry Product Protocol
Revision: June 6, 1995

6. Test Conditions
6.1 The two sets of test conditions are listed below. One of the chambers is maintained at the typical conditions and the other at the high-end conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Typical</th>
<th>High-End</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>70 F (21.1 C)</td>
<td>80 F (26.7 C)</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>50 percent</td>
<td>50 percent</td>
</tr>
<tr>
<td>Air Exchange Rate</td>
<td>1 per hour</td>
<td>0.3 per hour</td>
</tr>
<tr>
<td>Product Loading</td>
<td>Normal</td>
<td>Normal</td>
</tr>
</tbody>
</table>

The normal chamber loadings (in m² of surface area/m³ of chamber volume) defined for various products in these tests are listed in Table 1. These loading rates are based on an information survey conducted for the purpose of selecting products for testing, and on other factors. A description of the rationale behind the loading rates shown in Table 1 is given in Appendix A of this protocol. All products are tested one at a time, i.e., no combinations of products are tested.

7. Hazards
7.1 Normal care is required in laboratory procedures with both the DNPH and the real-time formaldehyde methods. Acetonitrile is required in the DNPH method, and should always be used with adequate ventilation, and with precautions to avoid skin exposure. Acetylacetonate (i.e., 2,4-pentanedione) is used in small quantities in the real-time method; use with caution and avoid skin contact.

8. Sample Storage
8.1 The aim of this protocol is to conduct chamber tests in a reproducible manner on samples that are realistic in terms of the products actually used in California residences. As a result, sample storage before chamber testing is intended to prevent cross-contamination of samples and to minimize decay of formaldehyde emission before testing. Samples are subjected to chamber testing no more than one month after receipt at Battelle. During the period of storage, samples are held in a secure area, under normal temperature and humidity conditions (i.e., 73 +/- 5 F; 50 +/- 5 percent RH). The storage area will have a formaldehyde level no higher than 50 ppbv during the storage period.
8.2 All samples obtained in packaged form will be stored in their original packaging until tested. Samples not ordinarily obtained in packaged form, such as wood products, will be shipped to Battelle wrapped in plastic film. The film wrapping will remain in place until a few days before testing, at which time the samples are removed for trimming and edge sealing.
8.3 Samples will be shipped to Battelle in standard sizes (e.g., 2 ft x 2 ft), and trimmed as required to the sizes needed for testing.
9. Test Procedure

9.1 Chamber Background: Purge the chambers with humidified Aadco air before and between materials tests to maintain a chamber formaldehyde background level of 10 ppbv or less. Clean the chamber surfaces with water after each test, or as needed to maintain the background level.

9.2 Edge Sealing: Prior to testing, seal the edges of any product samples for which the edge area is more than about 0.5 percent of the total product surface area. Edge sealing is done by applying a coat of sodium silicate solution (i.e., "water glass") to all edge areas. Allow the coating to dry in the open air for two days before placing the sample in the chamber.

9.3 Loading the Chambers: Place test samples in the chambers at the required loading rates so that they are not in the direct air flow from the mixing fans, and do not obstruct the air flow.

9.4 Chamber Conditions: Operate the two chambers at the test conditions indicated in section 6. Continuously monitor the air flow, temperature, and humidity in the chambers, and record the values either continuously or as often as needed to document stability of conditions.

9.5 Test Period: Place test samples in the chambers prior to 12:00 noon on the day of chamber testing. In general, samples remain in the chambers for 20 hours before sampling with DNPH for formaldehyde and other compound determination (i.e., until at least 8 a.m. the next morning). This time period is more than sufficient for formaldehyde levels to reach steady state in the chamber. However, for some low-emitting samples (such as fabrics, insulation, or paper products), depletion of the formaldehyde emissions before completion of a 20-hour test may be of concern. As a result, the real-time formaldehyde data are used to define the appropriate time for DNPH sampling, as described below.

9.6 Real-Time Sampling: The real-time measurement of formaldehyde in the chamber is used to document the approach to steady state concentrations, and to observe the emission behavior of the diverse products tested. Begin real-time measurements prior to placing test samples into the chambers, to determine the chamber background level. Switch the sampling inlet of the monitor from one chamber to the other periodically to obtain adequate measurement of formaldehyde in both chambers. For samples that show steady state formaldehyde concentrations, performance of the DNPH sampling at the end of the 20-hour period is appropriate. However, if the real-time data indicate a decay of formaldehyde concentrations during the test, DNPH sampling should be initiated at such time that concentrations are no more than 20 percent below the peak concentration.

Operation of the real-time monitor during all tests is desirable. However, should the monitor be unavailable, in a few specific instances tests may be conducted without the monitor. Such instances include (e.g.) the final tests of a series of wood products for which achievement of steady state concentrations has already been demonstrated, or performance of the second in a set of duplicate tests for which the monitor has already been used in the first test.

9.7 DNPH Sampling: Quantitative emission rates for dry products will be based on DNPH sample results. DNPH sampling is to be performed either at the completion of a 20-
hour chamber test, or at a time indicated by the real-time data. First draw chamber air
through the sampling lines for 5 minutes to purge them. Then collect two simultaneous
samples using the DNPH method. Each sample is collected by drawing chamber air
through an impinger containing 20 ml of DNPH/acetonitrile solution, at a flow rate of 1 liter
per minute for 30 to 60 minutes. A single DNPH sample should also be taken before
introduction of the sample into the chamber, to allow correction for chamber background.

9.8 DNPH Analysis: Perform analysis of the DNPH samples for formaldehyde and
other aldehydes by high pressure liquid chromatography, as prescribed in EPA Method TO-
5. Correct the test results for the chamber background, using the pre-test DNPH sample.

9.9 Emptying the Chambers: At the completion of the DNPH sampling, open the
chambers and remove the test samples. Close the chamber doors and allow the empty
chambers to purge with Aadco air. Repeat steps 9.1 to 9.9 as necessary for other products.

9.10 Comparison Tests: For two wood products (one urea-formaldehyde
particleboard and one hardwood plywood) conduct tests both as stated above for the 1.43 m³
chambers, and at the Typical test conditions shown above, using Battelle's 17.3 m³ chamber.
Use the same product loading rates in the large and small chambers.

9.11 Quality Control: All chamber tests, sampling and analysis must follow the
quality control guidelines set out in the accompanying Quality Assurance Program Plan for
this study.

10. Calculations

10.1 Calculations of the measured chamber concentrations are conducted in a manner
analogous to that prescribed in section 11 of the ASTM large chamber method. However,
chamber formaldehyde concentrations are reported to the nearest 1 ppbv, as are the
concentrations of other carbonyl compounds measured. Calculation of concentrations from
the real-time data is based on calibrations of the monitor with standard solutions of known
formaldehyde content.

10.2 Corrections of the concentration values for temperature and relative humidity
are applied for wood product results, as described in the ASTM procedure, only if the
chamber temperature or relative humidity deviate from the test conditions by more than 1
degree F or 2 percent RH, respectively, during the last hour before DNPH sampling or
during the DNPH sampling itself.

10.3 The formaldehyde surface emission rates of the test samples are calculated as
follows:

\[ E = C \times N/L \]

where

\( E \) = surface formaldehyde emission rate, in \( \text{ug/m}^2/\text{hr} \)
\( C \) = formaldehyde chamber concentration, in \( \text{ug/m}^3 \)
\( N \) = chamber air exchange rate, \( \text{hr}^{-1} \)
\( L \) = sample loading rate, in \( \text{m}^2/\text{m}^3 \)
11. Reporting

11.1 The test results are reported in a summary final report on the study. That report must follow the specific guidelines set forth by CARB. In general, the information to be reported includes data on the tested materials, the test procedures, the analytical method, and the test results.

11.2 Tested Materials: To the extent possible, report information defining the nature and origin of the tested samples. Such information includes the manufacturer, supplier, lot or production number, date of manufacture or product history, type of product, dimensions, and surface treatment or lamination.

11.3 Test Procedures: Report the manner in which the test samples were shipped and stored before testing, including any packaging of samples for shipment, edge sealing, and the formaldehyde level in the storage area. Document the chamber characteristics and actual test conditions, including loading rates, air exchange rates, temperature, relative humidity, and background formaldehyde level.

11.4 Analytical Method: Report the characteristics and QC results of the methods used. Describe the results of any evaluations of the method's accuracy, precision, or bias. Report analytical results for other compounds measured besides formaldehyde.

11.5 Test Results: Report both the chamber formaldehyde concentrations and the calculated emission rates for both test conditions for all products tested. Discuss comparisons of the results from the two test conditions, from the various product types, and within product types.

12. Precision and Bias

12.1 The repeatability of the chamber procedure is likely to be comparable to that noted in the ASTM documentation. Chamber test results on identical samples are expected to agree within about 10 percent.

12.2 The EPA TO-5 DNPH method for formaldehyde has been compared to the NIOSH 3500 chromatropic acid method and found to give essentially the same results. The precision of replicate analyses is within about 5 percent. Considering errors in flow measurements, the precision of simultaneous DNPH samples in the chamber tests is expected to be within about 8 percent.

12.3 The continuous real-time formaldehyde monitor has been validated by comparison with the DNPH method, and with the pararosaniline continuous monitor, at formaldehyde concentrations of 1 to 100 ppbv. For example, a linear regression of 11 DNPH samples, collected in outdoor air at formaldehyde concentrations up to 4 ppbv, with the corresponding real-time data gave the following result: Real-Time Formaldehyde = 1.29 (+/- 0.33) [DNPH Formaldehyde] - 0.04 (+/- 0.49) ppbv. Agreement of the same two methods at levels above 20 ppbv was generally within 15 percent. Similar agreement has been reported in a comparison with an enzyme-based sensor at formaldehyde concentrations below 4 ppbv in ambient air.
13. References


Table 1: Loading Rates for Testing of Products in Battelle's 1.43 m³ Chambers

<table>
<thead>
<tr>
<th>Product Category/Identity</th>
<th>Loading Rate (m²/m³)ᵃ</th>
<th>Required Surface Area (m²)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Urea-Formaldehyde Wood Prods.</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particleboard</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5/8&quot; Underlayment</td>
<td>0.46</td>
<td>0.65ᶜ</td>
</tr>
<tr>
<td>5/8&quot; Mobile Home Decking</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>3/4&quot; Industrial Particleboard</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>5/8&quot; Industrial Particleboard</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>3/4&quot; I.P., melamine laminate - domestic</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>3/4&quot; I.P., melamine laminate - imported</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>5/8&quot; I.P., vinyl coated</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>5/8&quot; I.P., &quot;Cortron&quot; coated</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>Interior Door with I.P. Core</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td><strong>Medium Density Fiberboard</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/4&quot; MDF - un laminated</td>
<td>0.26</td>
<td>0.37ᵈ</td>
</tr>
<tr>
<td>3/4&quot; MDF - UV cured filler</td>
<td>0.26</td>
<td>0.37</td>
</tr>
<tr>
<td>3/4&quot; MDF - melamine laminate</td>
<td>0.26</td>
<td>0.37</td>
</tr>
<tr>
<td><strong>Hardwood Plywood</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/4&quot; Stock Plywood</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>1/4&quot; Prefinished Wall Panelling</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>1/4&quot; Stock Plywood</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>1/2&quot; Stock Plywood</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>1/2&quot; Hardwood Veneer Plywood</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td><strong>Hardboard</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/4&quot; Hardboard Sheet</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>1/4&quot; Perforated Hardboard</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td><strong>Phenol-Formaldehyde Wood Prods.</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/4&quot; Oriented Strand Board</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>3/4&quot; Softwood Plywood</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td>3/4&quot; Exterior Particleboard</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td><strong>Decorative Laminates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 mil General Purpose</td>
<td>1.8</td>
<td>2.61ᵉ</td>
</tr>
<tr>
<td>50 mil General Purpose</td>
<td>1.8</td>
<td>2.61</td>
</tr>
<tr>
<td>20 mil Cabinet Liner Type</td>
<td>1.8</td>
<td>2.61</td>
</tr>
</tbody>
</table>
Table 1: (Continued)

<table>
<thead>
<tr>
<th>Product Category/Identity</th>
<th>Loading Rate (m²/m³)</th>
<th>Required Surface Area (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fabrics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permanent Press Shirts</td>
<td>3.25</td>
<td>4.65</td>
</tr>
<tr>
<td>Permanent Press Sheets</td>
<td>3.25</td>
<td>4.65</td>
</tr>
<tr>
<td>Permanent Press Draperies</td>
<td>3.25</td>
<td>4.65</td>
</tr>
<tr>
<td><strong>Insulation Products</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fiberglass Ceiling Panels</td>
<td>1.0</td>
<td>1.49</td>
</tr>
<tr>
<td>Fiberglass Roll Insulation</td>
<td>1.0</td>
<td>1.49</td>
</tr>
<tr>
<td><strong>Coatings/Paints</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commercially Applied Acid-Cured Cabinet Finish</td>
<td>0.46</td>
<td>0.65</td>
</tr>
<tr>
<td><strong>Paper Products</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paper Towels</td>
<td>1.0</td>
<td>1.49</td>
</tr>
<tr>
<td>Paper Grocery Bags</td>
<td>1.0</td>
<td>1.49</td>
</tr>
</tbody>
</table>

(a): The loading rates shown are based on competing factors of 1) realism, 2) comparability among products and tests, 3) detectability of emissions, and 4) consistency and simplicity of sample sizes needed. See Appendix A below for discussion of these factors and the loading rates shown in Table 1.

(b): Area shown is total exposed surface area of product needed in each 1.43 m³ chamber, including both sides of the sample.

(c): This surface area is provided by both sides of a 22.5 in x 22.5 in sample.

(d): This surface area is provided by both sides of a 12 in x 24 in sample.

(e): This surface area is provided by both sides of four 22.5 in x 22.5 in sample pieces.

(f): This surface area is provided by both sides of a 5 ft x 5 ft fabric sample. A sample of that size will be cut from draperies and sheets; shirts will be used uncut, in quantities needed to achieve the desired surface loading rate.

(g): This surface area is provided by both sides of a 2 ft x 4 ft standard ceiling panel, or by equivalent areas of other insulation or paper products.
APPENDIX A: RATIONALE FOR SELECTION OF PRODUCT LOADING RATES FOR CHAMBER TESTS

The loading rates and required product surface areas shown in Table 1 were established based on consideration of several factors. The factors that were considered are described below, and the reasoning behind the values shown in Table 1 is then presented. Note that the references indicated here are those listed at the end of this appendix, and not those listed on page 8 of this protocol.

Realism: For estimation of human exposure to formaldehyde emissions from the indicated products, it would be valuable to conduct chamber tests at loading rates that mimic those in homes and apartments. This would mean testing products at a wide variety of loading rates, because of the different extent of use of various products in residences. For some products, loading rates pertinent to individual rooms or areas of use might be more useful than whole-home loading rates.

Comparability: This factor has two different meanings. One is the extent to which chamber tests in this program can be compared to standard test procedures used by industry. Examples of the latter are the ASTM large chamber test procedure used for evaluating formaldehyde emissions from wood products,\(^1\) which is the basis for ANSI standards for medium density fiberboard\(^2\) and for particleboard,\(^3\) and the FTM-2 procedure\(^4\) referenced by the U.S. Department of Housing and Urban Development (HUD) for testing of particleboard and plywood used in manufactured homes. Comparability with these procedures primarily means using the same loading rates and chamber conditions as in the standard tests. In general, the standard tests often use loading rates that exceed realistic loadings in homes.\(^5\)

The other meaning of comparability is the degree to which the test procedure allows comparisons to be made between widely different product types. This meaning is the more important of the two for the present program, because the aim of this program is to determine the relative importance of diverse product types in causing formaldehyde exposures in residences. Since the test conditions are fixed in this program, comparability between various product types depends primarily on using similar loading rates, or at least loading rates that allow comparable accuracy in determination of emission rates.

Detectability: As described in the product selection document for this program,\(^5\) the products to be tested are likely to have formaldehyde emission rates that cover a wide range. In order to quantify the emission rates of the products tested, loading rates must be high enough to produce increases in chamber formaldehyde levels that are clearly detectable by the real-time and DNPH methods. In the face of chamber background concentrations the minimum detectable change is estimated to be about 1 ppbv with both methods, though the absolute detection limits of the methods are lower than that. However, a minimum change equivalent to the maximum allowable chamber background (i.e., 10 ppbv) would be preferable for quantitation. Based on these minimum requirements, calculations indicate that for some products expected to have low emission rates the realistic in-home loadings may not produce a detectable increase in chamber formaldehyde concentrations. For such products, unrealistically high loading rates may be necessary in order to accurately determine the formaldehyde emission rate.
Sample Sizes: Advantages exist in simplicity of product preparation and consistency of testing when the same loading rates are used for several products. Products to be tested will be obtained in California and shipped to Battelle for testing. In many cases, large items such as wood products will be cut to appropriate sample sizes before shipping. Greater efficiency and reduced chance of error occurs when the shipper can prepare many samples in the same sample sizes. The consistency of test procedures is also improved by this approach, since consistent sample sizes means that the same positioning and sample holding techniques can be used in many tests.

Rationale for Loading Rates in Table 1

The factors above were considered jointly in establishing the planned loading rates shown in Table 1. The factors of realism and comparability were given the greatest weight, because of their importance to the overall aims of this project. As a result, realistic loading rates were chosen for as many products as possible, within the bounds of achieving detectable concentration changes in the chambers. The detectability factor was judged subjectively, since for most product types very few data are available with which to estimate product emission rates. Finally, in the interests of efficiency, loading rates that were similar were made equal to one another, to simplify the range of product sample sizes needed.

The loading rate for the particleboard products in Table 1 are a compromise between the factors of realism and comparability. The loading rate of 0.46 m²/m³ shown for mobile home decking and industrial particleboard is a realistic in-home rate. In order to directly compare other particleboard products with these products, it is reasonable to use the same loading rates. Thus underlayment has the same loading rate as decking, and the coated or laminated particleboard products have the same loading rate as the raw (uncoated) particleboard. Using the same loading rates for the latter products will allow the most direct comparison of the effect of coatings on formaldehyde emissions. The loading rate of 0.46 requires only both sides of a 22.5 in x 22.5 in piece of material in each chamber.

The loading rates for MDF reflect two factors. First, the 0.26 loading is stated in the ANSI MDF specification for chamber testing. Second, this loading rate was indicated as a realistic in-home rate in the product selection process. Given the expected relatively high emission rate of MDF, the 0.26 loading is sufficient to meet the criteria of detectability.

Loading rates listed in Table 1 for hardwood plywood and hardboard are defined primarily for comparability and detectability. The 0.46 loading rate is realistic for stock hardwood plywood, but not necessarily for other products such as wall panelling. However, this loading rate will allow direct comparability among the hardwood plywood products, and between hardwood plywood and particleboard products. The same 0.46 loading rate is planned for hardboard, even though this rate greatly exceeds the likely in-home loading of this product. This loading rate is justified, however, by the expected very low emission rate of hardboard. An exaggerated loading is needed to assure accurate measurement of the emission rate, and the 0.46 value also will allow direct comparison of hardboard emissions to those of other wood products.
Comparability and detectability also drive the planned 0.46 loading rate for the P-F wood products. That loading rate is reasonably realistic for softwood plywood, though not for OSB or possibly for exterior particleboard. However, the emission rates of the P-F products are expected to be much lower than those of the U-F products, so an exaggerated loading is appropriate to allow accurate measurements and direct comparison of the U-F and P-F products.

The loading rate shown in Table 1 for decorative laminates is a realistic rate for the kitchen area of a home or apartment, where use of this material is concentrated. The few previous emission data for this product show low emissions, so use of this relatively high rate will aid in measurement of the emission rate.

The primary factor in establishing the loading rates for fabric products is detectability. Emission rates from these products are expected to be low, even for new products. In addition, the thin surface coatings on fabric products may result in a rapid decay of the emission rate. It is not known whether such decay may occur within the time period of a chamber test, but in any case use of a relatively elevated loading rate will promote accurate measurement of emissions. In general, the loading rate shown for fabrics in Table 1 is elevated relative to whole-house loadings, but may be realistic for small parts of the home or storage areas where fabric products are concentrated. The close proximity of some fabric products (i.e., clothing, bedding) to the user enhances any exposure to formaldehyde, and also justifies the use of elevated loading rates. For clothing, it was desirable to test the entire product, because testing will also be conducted after the product is washed. Damage to the samples might result in washing if only precut portions, rather than the entire garments, were tested. As a result, the loading rate for clothing will be achieved using entire garments.

Detectability, comparability, and simplicity of testing were key considerations for insulation products. Like decorative laminates and fabrics, these products are expected to have relatively low emission rates. The loading rates shown for insulation products exceed the realistic loading rates by about a factor of 10. The loading rate shown for ceiling insulation panels is based on achieving a substantial loading rate with the standard 2 ft x 4 ft size of panels. The loading rate shown for roll insulation is the same, to assure comparability of results between these two products. It is anticipated that a standard ceiling panel may be cut in half to produce 2 ft x 2 ft pieces for delivery to Battelle.

The category of coatings and paints refers here only to finished acid-cured coatings applied by a commercial manufacturer of cabinets. Testing will be conducted with coated and uncoated cabinet doors. The loading rate shown is based on both sides of a standard cabinet door. The 0.46 loading rate shown will allow direct comparison of results from fresh acid-cured coatings to those from the various coated and uncoated wood products. Based on information at hand, detection of emissions from the acid-cured coatings should be readily achievable at the loading rate shown, especially with fresh coatings.

Finally, the loading rate shown for paper products is determined primarily by the detectability factor. The paper products considered in this test protocol are paper towels and bags. Formaldehyde emissions from these products are expected to be minimal at best, so the elevated loading shown is needed to assess the emission rate. The loading rate shown
Dry Product Protocol
Revision: June 6, 1995

greatly exceeds the likely in-home loadings for these products, but is similar enough to the
loadings for other product types that comparability of emission rates will be preserved.

Only five different loading rates are planned (0.26, 0.46, 1.0, 1.8, and 3.25 m²/m³). These
loadings are readily achieved with sample pieces of moderate dimensions. For most
products, the requisite sample sizes (e.g., 22.5 in x 22.5 in) will be achieved by trimming
of standard 2 ft x 2 ft pieces in Battelle’s shop. The latter 2 ft x 2 ft size is an attractive
nominal size in which to procure samples in the field. That size is small enough to be
shipped easily, even when sample pieces are layered in with waster sheets for protection in
shipping. The uniformity of the sample sizes needed will promote speed and efficiency in
obtaining the requisite samples for testing.

References for Appendix A
1. Standard Test Method for Determining Formaldehyde Levels from Wood Products Under
Defined Test Conditions Using a Large Chamber, Designation E-1333-90, American Society
1990.

2. American National Standard: Medium Density Fiberboard (MDF), ANSI A208.2-1994,
published by National Particleboard Association, Gaithersburg, Maryland, 1994.

Particleboard Association, Gaithersburg, Maryland, 1993.

4. Large Scale Test Method for Determining Formaldehyde Emissions from Wood Products,
Large Chamber Method, FTM 2-1985, prepared by the National Particleboard Association

5. Selection of Products for Chamber Testing, Interim Report to California Air Resources
Board, Project No. 93-315, prepared by Battelle, Columbus, Ohio, March 1995.
APPENDIX C

PROTOCOL FOR CHAMBER TESTING OF FORMALDEHYDE EMISSIONS FROM "WET" PRODUCTS USED IN RESIDENCES

The document shown in this Appendix was prepared during the course of Research Project 93-315, and served as the basis for a portion of the project. However, the main body of this report should be consulted as the most complete and final presentation of the study activities and results.
PROTOCOL FOR CHAMBER TESTING OF FORMALDEHYDE EMISSIONS FROM "WET" PRODUCTS USED IN RESIDENCES

California Air Resources Board Project 93-315

prepared by
Battelle
505 King Avenue
Columbus, Ohio 43201-2693

Revision Date: June 29, 1995

1. Scope

1.1 This protocol states the procedures to be used for testing of formaldehyde emissions from paints, coatings, and other products used in residences, as part of the California Air Resources Board project identified above. Emissions from such sources are determined by application to test surfaces, and subsequent measurements of formaldehyde concentrations in medium-size chambers, under conditions of controlled temperature, humidity, and air flow. This protocol employs a continuous real-time monitoring method for formaldehyde,\(^1\) to track the decay of formaldehyde emissions during the drying of the products. The formaldehyde content of chamber air is also determined by the 2,4-dinitrophenylhydrazine (DNPH) method (U.S. EPA Compendium Method TO-5). Other analytical procedures may be used if they provide formaldehyde results comparable to those from the DNPH procedure, however, the DNPH method also provides measurement of other carbonyl compounds in the same analysis. Additional compounds to be determined by the DNPH method in this study include acetaldehyde (which is listed in both the 1990 Clean Air Act Amendments list of Hazardous Air Pollutants (HAPs) and in California’s Proposition 65 list of chemicals), and propionaldehyde, methyl ethyl ketone, and methyl iso-butyl ketone (which are all on the HAPs list).

1.2 This protocol calls for performance of emission tests at two separate test conditions in twin chambers, each maintained at one of the two conditions. This approach offers advantages in efficiency and precision of test performance. However, performance of the tests in a single chamber by sequentially adjusting test conditions may also be suitable, provided that such an approach provides reproducibility of test conditions and test results comparable to those obtained with separate chambers.

1.3 The protocol stated here is designed for testing of "wet" products, i.e., those that need an application, spraying, or drying step to simulate normal use. The products for which this protocol is intended include paints, floor coatings, cosmetics (i.e., nail hardeners and polishes), and wallpaper. The chamber conditions and loading rates for testing of these products are specified in this protocol. The general procedure described here may be applied to other similar products not specifically named, provided the test results are properly documented with the loading rates and test conditions used.

1.4 A separate test protocol exists for testing of "dry" products in this study. Those products include wood products, decorative laminates, insulation, fabrics, and paper products.

1.5 Hazards associated with the samples and chemicals used in this protocol are stated in section 7. However, this protocol does not purport to address all of the potential
safety issues resulting from its use. The user of this protocol is responsible for establishing safe operating conditions and procedures.

2. References

2.1 Published documents that are the basis for this protocol are cited by means of Arabic numeral superscripts, and are listed in numerical order at the end of this document.

3. Terminology

3.1 The terms used in this protocol are common in the field of chamber testing. The reader is referred to standard chamber test procedures (e.g., 2,3) for background on the terms used.

4. Significance and Use

4.1 This test protocol is specifically designed for the performance of chamber tests by Battelle for the purposes of the CARB project cited above. The aim of this project is to obtain formaldehyde emission rate data for a wide variety of products used in homes in California. The results of this project are intended to update similar test results obtained a decade or more ago by the Consumer Product Safety Commission.(4,5) The test results will allow CARB to inform the public as to what are the most important indoor formaldehyde sources, with the goal of reducing the indoor formaldehyde exposure of the California populace.

4.2 The test protocol uses twin stainless steel and glass chambers of 1.43 m³ volume, for testing at two sets of conditions. The chamber temperature, humidity, air exchange rate, and internal mixing are controlled. Product loading rates, i.e., the exposed surface area of the material tested per unit volume of the chamber, are also specified for the various products. Constant conditions are maintained in the chambers during the drying of the freshly applied products, while the chamber air is sampled for determination of formaldehyde and other aldehydes.

4.3 The two sets of test conditions are representative of typical and high-end indoor conditions, in terms of the temperature and air exchange rates. The intent of this selection is to bracket the emission rates to be expected in homes.

4.4 Although the test procedures are designed to provide emission rates that are realistic relative to those that may occur in a home, caution must be used in extrapolating the test results to any real home or to other test conditions. The test results are primarily intended to allow comparison of different product types.

5. Apparatus

5.1 Test Chambers: Tests are conducted in two chambers located side-by-side in Battelle's laboratories. Each chamber has a volume of 1.43 m³, and is built of stainless steel and glass. The front face of each chamber is a door of 80 cm x 125 cm dimensions, consisting of a nearly full size glass pane in a steel frame. The doors are self-sealing by means of elastomer seal strips which are minimally exposed to air within the chamber once the door is closed. External clamps on the circumference of the doors assure a proper seal
during testing. Steel mesh shelving can be positioned at several vertical locations for support of test samples in the chambers.

5.2 Internal Mixing: A fan is located near the top of each chamber to promote mixing of air within the chamber. These fans are driven by electric motors located outside the chambers. The air movement from the fan is partially obstructed by a baffle so that air flow is not directly at the test samples.

5.3 Clean Air Supply: The air flow into the chambers is provided by an Aadco pure air generation system, which removes water vapor, particulate matter, and gaseous contaminants from outdoor ambient air. The formaldehyde content of the air from this supply is less than 0.1 ppbv (0.12 micrograms per cubic meter, ug/m³), and the total content of other organic contaminants is less than 20 ppbv. The flows of dry and humidified Aadco air into the chambers are controlled by mass flow controllers of 10 to 30 L/min capacity (Tylan or comparable). Those flowmeters are calibrated at regular intervals (independent of this study) by comparison to known flow standards in Battelle's central Instrument Laboratory. The test chambers operate at a slight positive pressure, i.e., < 0.2 psig, which is monitored by Magnelhelic gauges. Air leaving the chambers is drawn into a vacuum duct and is exhausted into a laboratory hood and subsequently outdoors.

5.4 Air Sampling Ports: Each chamber is equipped with several ports suitable for sampling. Air sampling is conducted by extending a Teflon sampling tube (6 mm O.D. or similar) to about the midpoint of the chamber, but no closer than 30 cm from any surface of the test sample. Sampling apparatus is located on tables next to the chambers, assuring that sampling lines are as short as possible.

5.5 Air Sampling and Analysis Methods: Continuous real-time formaldehyde measurements are made with a monitor developed by Battelle under EPA support.¹,⁶ That monitor employs continuous collection and derivatization of formaldehyde, using continuous fluorescence as the final analytical technique. The monitor draws a sample air flow of 2 L/min, and has full scale ranges from 20 ppbv to 20 ppmv. The lag time and rise time of the monitor are 2 minutes and 1 minute, respectively. Details of the operation of this instrument have been published.¹

Determination of formaldehyde (and other aldehydes) is also accomplished using EPA Compendium Method TO-5, which involves impingers containing DNPH in acetonitrile solution. The real-time formaldehyde data are used to define the time of DNPH sampling during each test. DNPH samples are taken when the real-time data indicate that formaldehyde levels have stabilized in the chamber, or when the real-time data show it to be necessary to achieve proper detection of the target compounds. Details of the DNPH method can be found in the appropriate EPA document.⁷

6. Test Conditions

6.1 The two sets of test conditions are listed below. One of the chambers is maintained at the typical conditions and the other at the high-end conditions.
The normal chamber loadings (in m² of surface area/m³ of chamber volume) defined for various products in these tests are listed in Table 1. These loading rates are based on an information survey conducted for the purpose of selecting products for testing. The loading rates shown in Table 1 represent those in a room where the products are being applied, and consequently where consumer exposure is greatest. Additional tests at higher loading rates will be conducted, as described in section 9, if the indicated rates provide a formaldehyde level too low for accurate determination.

7. Hazards
7.1 Normal care is required in laboratory procedures with both the DNPPh and the real-time formaldehyde methods. Acetonitrile is required in the DNPPh method, and should always be used with adequate ventilation, and with precautions to avoid skin exposure. Acetylaceton (i.e., 2,4-pentanedione) is used in small quantities in the real-time method; use with caution and avoid skin contact.
7.2 The wet products tested by this procedure may contain volatile and/or toxic chemicals, or may be flammable. Follow all directions on the product label for proper storage, application, and disposal.

8. Sample Storage
8.1 The aim of this protocol is to conduct chamber tests in a reproducible manner on samples that are realistic in terms of the products actually used in California residences. As a result, sample storage before chamber testing is intended to prevent cross-contamination of samples and to minimize decay of formaldehyde emission before testing. Samples are subjected to chamber testing no more than one month after receipt at Battelle. During the period of storage, samples are held in a secure area, under normal temperature and humidity conditions (i.e., 73 +/- 5 F; 50 +/- 5 percent RH). The storage area will have a formaldehyde level no higher than 50 ppbv during the storage period.
8.2 All samples obtained in packaged form will be kept in their original packaging until tested. Wallpaper will be wrapped in plastic film, which will remain in place during storage until the time of testing.

9. Test Procedure
9.1 General: In this procedure a product is tested simultaneously in the two chambers, with the real-time formaldehyde monitor sampling alternately from the two chambers. This approach allows rapid determination of the formaldehyde emission and decay with the real-time monitor, for each product in each set of test conditions.
Wet Product Protocol
Revision: June 29, 1995

9.2 Chamber Background: Purge the chambers with humidified Aadco air before and between materials tests to maintain a chamber formaldehyde background level of 10 ppbv or less. Clean the chamber surfaces with water after each test, or as needed to maintain the background level.

9.3 Chamber Conditions: Operate each chamber at the appropriate test conditions, as indicated in section 6. Continuously monitor the air flow, temperature, and humidity in the chambers, and record the values either continuously or as often as needed to document stability of conditions.

9.4 Test Surfaces: Prepare a test surface of the appropriate size and material for the product to be tested, as indicated in Table 1. Test surfaces must be clean and previously unused.

9.5 Product Application (Paints, coatings, and nail finishes): Prior to 12:00 noon on the test day, apply the product to the test surface outside the test chamber, under normal room conditions. Application should be done at least several feet away from the test chambers, and preferably on the far side of the laboratory containing the two test chambers, where a fume hood will draw direct emissions from the open product container out of the laboratory. Open the product container and mix the product according to the manufacturer’s instructions until thoroughly mixed. Dispense the product from a graduated cylinder, buret, or similar apparatus to provide an approximate measure of the amount of product applied to the test surface. Apply the product to the test surface using a brush or roller, applying only enough product to achieve coverage of the surface. Avoid over-application, and wipe any excess off the edges of the test surface with a clean cloth. Close the product container immediately after application of the product. Within one minute after completion of product application, open the chamber door, place the test sample in the center of the chamber, and close the door tightly. Immediately record the time at which the door was closed, as the start of the test.

9.6 Product Application (Wallpaper): Prior to 12:00 noon on the test day, apply the product to the test surface outside the test chamber, under normal room conditions. The wallpaper to be tested is paper-based and pre-pasted. Cut a piece or pieces of the dry wallpaper of appropriate size to cover the test surface area (Table 1). Immerse the wallpaper in clean water for sufficient time to soften the paste, according to the manufacturer’s instructions for application. Position the wallpaper on the test surface and smooth it flat with a wallpaper brush. Wipe any water or excess paste off the test surface with a clean, damp cloth or lint-free laboratory towel. Within one minute after completing the application, open the chamber door, place the test sample in the center of the chamber, and close the door tightly. Immediately record the time at which the door was closed, as the start of the test.

9.7 Real-Time Sampling: Operate the continuous real-time formaldehyde monitor during all chamber tests, sampling alternately from each chamber for 5-minute periods, by means of an automated switching valve. Begin real-time measurements prior to introducing the product into the chamber, to determine the chamber background levels. Continue the real-time measurements for at least 20 hours (i.e., until about 8 a.m. on the day following the start of the test). If formaldehyde levels at that time are continuing to decay, and still exceed 25 percent of the peak formaldehyde levels observed at the start of the test, then
continue real-time sampling, up to a maximum test period of 48 hours. If at any point at or beyond 20 hours into the test the formaldehyde concentrations appear to have stabilized (i.e., the relative change over an hourly period is less than 5 percent), the test may be terminated after completion of DNPH sample collection (see section 9.8).

Record the real-time formaldehyde data, along with the chamber temperature and relative humidity data, on a PC-based data system. Fit the recorded real-time data with a first-order decay model, as described below, to determine the wet product emission characteristics.

9.8 DNPH Sampling: Ideally, sampling with the DNPH method should be performed at a time during the chamber test when formaldehyde concentrations are sufficiently stable for integrated sampling to be effective. To accomplish this, the timing of DNPH sampling is to be selected by the test personnel based on the real-time formaldehyde data, as defined in section 9.7. However, if chamber formaldehyde concentrations (as indicated by the real-time monitor) approach minimum detectable levels with no sign of levelling off, DNPH sampling should be initiated to assure accurate measurements. Following completion of DNPH sampling, the test is terminated. DNPH sampling is to be conducted by first drawing chamber air through the sampling lines for 5 minutes to purge them. Then collect two simultaneous samples using the DNPH method.(7) Each sample is collected by drawing chamber air through an impinger containing 20 ml of DNPH/acetonitrile solution, at a flow rate of 1 liter per minute for 30 to 60 minutes. A single DNPH sample should also be taken before introduction of the sample into the chamber, to allow correction for the chamber background.

9.9 DNPH Analysis: Perform analysis of the DNPH samples for formaldehyde and other aldehydes by high pressure liquid chromatography, as prescribed in EPA Method TO-5.(7) Correct the test results for the chamber background, using the pre-test DNPH sample.

9.10 Repeat Tests: The realistic chamber loading rates for some wet products, notably nail hardeners and polishes, are very low (Table 1). For these products, the real-time data will be reviewed to determine whether formaldehyde release at the normal loading rate was sufficient for accurate measurement. If formaldehyde concentrations during a test are near the detection limit of the real-time monitor, the test may be terminated and a repeat test conducted with a loading rate 10 times larger than that shown in Table 1.

9.11 Emptying the Chambers: At the completion of the test, open the chambers and remove the test materials. Close the chamber doors and allow the empty chambers to purge with Aadcio air. Repeat steps 9.1 to 9.9 as necessary for other products.

9.12 Quality Control: All chamber tests, sampling and analysis must follow the quality control guidelines set out in the accompanying Quality Assurance Program Plan for this study.(9)

10. Calculations

10.1 Calculations of the measured chamber concentrations are based on calibrations of the continuous monitor with standard solutions of known formaldehyde content.(9) Calculation of additional data from the DNPH method is conducted in a manner analogous to that prescribed in section 11 of the ASTM large chamber method.(2) However, chamber
formaldehyde concentrations are reported to the nearest 1 ppbv. The concentrations of additional carbonyl compounds determined by the DNPH method are also calculated in an analogous manner.

10.2 The formaldehyde surface emission rates of the test samples are calculated as described in section 9.4.2 of the ASTM guide.\(^{(3)}\) This approach approximates the decay of formaldehyde emissions from the product as a first-order decay, i.e.,

\[ R = R_0 e^{-kt} \]

where:
- \( R \) is the emission rate in \( \text{ug/m}^2/\text{hr} \)
- \( R_0 \) is the initial emission factor
- \( k \) is the first order decay constant, in \( \text{hr}^{-1} \)
- \( t \) is the time in hours.

Initial values of \( k \) and \( R_0 \) are estimated as described in the ASTM guide,\(^{(3)}\) and curve-fitting software is used to fit the data from the continuous monitor. The values of \( R_0 \) and \( k \), the value of the maximum formaldehyde concentration \( (C_{\text{max}}) \), and the time of occurrence of the maximum \( (t_{\text{max}}) \) characterize the product emissions.

11. Reporting

11.1 The test results are reported in a summary final report on the study. That report must follow the specific guidelines set forth by CARB. In general, the information to be reported includes data on the tested materials, the test procedures, the analytical method, and the test results.

11.2 Tested Materials: To the extent possible, report information defining the nature and origin of the tested samples. Such information includes the manufacturer, supplier, lot or production number, date of manufacture or product history, and type of product.

11.3 Test Procedures: Report the manner in which the test samples were shipped and stored before testing, including any packaging of samples for shipment, and the formaldehyde level in the storage area. Document the chamber characteristics and actual test conditions, including loading rates, air exchange rates, temperature, relative humidity, and background formaldehyde level.

11.4 Analytical Method: Report the characteristics and QC results of the method used. Describe the results of any evaluations of the method's accuracy, precision, or bias. Report analytical results for the other compounds measured besides formaldehyde.

11.5 Test Results: Report both the chamber formaldehyde concentrations and the parameters that characterize the emission rates for both test conditions for all products tested. Discuss comparisons of the results from the two test conditions, from the various product types, and within product types.

12. Precision and Bias

12.1 The repeatability of the chamber procedure is likely to be comparable to that noted in the ASTM documentation.\(^{(2)}\) Chamber test results on identical samples are expected to agree within about 10 percent.
Wet Product Protocol
Revision: June 29, 1995

12.2 The EPA TO-5 DNPH method for formaldehyde has been compared to the NIOSH 3500 chromototropic acid method and found to give essentially the same results. The precision of replicate analyses is within about 5 percent. Considering errors in flow measurements, the precision of DNPH samples in the chamber tests is expected to be within about 8 percent.

12.3 The continuous real-time formaldehyde monitor has been validated by comparison with the DNPH method, and with the pararosaniline continuous monitor, at formaldehyde concentrations of 1 to 100 ppbv.\(^1\) For example, a linear regression of 11 DNPH samples, collected in outdoor air at formaldehyde concentrations up to 4 ppbv, with the corresponding real-time data gave the following result: \( \text{Real-Time Formaldehyde} = 1.29 (+/- 0.33) [\text{DNPH Formaldehyde}] - 0.04 (+/- 0.49) \) ppbv. Agreement of the same two methods at levels above 20 ppbv was generally within 15 percent. Similar agreement has been reported in a comparison with an enzyme-based sensor at formaldehyde concentrations below 4 ppbv in ambient air.\(^10\)

13. References


C-8


Table 1: Loading Rates and Test Surfaces for Testing of Wet Products in Battelle's 1.43 m³ Chambers

<table>
<thead>
<tr>
<th>Product Identity</th>
<th>Loading Rate (m²/m³)ᵃ</th>
<th>Required Surface Area (m²)ᵇ</th>
<th>Surface Typeᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylacetate Latex Paint</td>
<td>1.0</td>
<td>1.49</td>
<td>Gypsum board</td>
</tr>
<tr>
<td>Acid-cured Floor Finish</td>
<td>0.41</td>
<td>0.59</td>
<td>Wood</td>
</tr>
<tr>
<td>Nail Hardeners</td>
<td>0.005</td>
<td>0.007ᵈ</td>
<td>Plasticᵉ</td>
</tr>
<tr>
<td>Nail Polish</td>
<td>0.005</td>
<td>0.007ᵈ</td>
<td>Plasticᵉ</td>
</tr>
<tr>
<td>Paper-based Wall Coverings</td>
<td>1.0</td>
<td>1.49</td>
<td>Gypsum board</td>
</tr>
</tbody>
</table>

(a): Loading rates shown represent those in a portion of the residence where the product is being used or applied.
(b): Surface area required in one chamber of 1.43 m³ volume.
(c): Clean material having the appropriate surface area shown must be used as the base to which product is applied for testing.
(d): Initial test to be conducted at this loading; if insufficient formaldehyde release occurs for accurate measurement, test will be repeated with 10 times higher loading rate.
(e): Test surface to be artificial fingernails or plastic sheet of equivalent polymer composition.
APPENDIX D

PROTOCOL FOR SCREENING OF CONSUMER PRODUCTS FOR EMISSION OF TOluene DIIsoCYANATE (TDI)

The document shown in this Appendix was prepared during the course of Research Project 93-315, and served as the basis for a portion of the project. However, the main body of this report should be consulted as the most complete and final presentation of the study activities and results.
1. Scope

1.1 This protocol is to be used in CARB Project No. 93-315, and states the procedures to be used in screening of consumer products for emission of toluene diisocyanates. The purpose of this screening is to assess whether TDI is released from polyurethane products in quantities sufficient to constitute a health risk. Products that show a release of TDI in these screening tests will then be subjected to more realistic tests, to assess the emissions that might occur under typical conditions in a residence.

1.2 Screening tests are conducted in a small glass chamber under elevated temperature conditions (approximately 120 degrees Fahrenheit). The presence of TDI in the chamber air, due to release from the products being tested, is determined by a continuous colorimetric monitor, and also by an impinger sampling/HPLC analysis method using N-(4-nitrobenzyl)-N-n-propylamine (NBPA) as a derivatizing agent. These methods were selected for this study by a comparison of the published characteristics of various methods for TDI determination. A summary of that comparison is presented as Appendix A of this report. The continuous monitor may be especially useful in tracking TDI emissions from polyurethane coatings and paints, and also provides a direct indication of chamber TDI levels for safety purposes. Alternative TDI measurement methods may be used for screening provided they have detection capabilities comparable to those of the NBPA and continuous methods.

1.3 The screening tests are conducted with exaggerated product loading rates to allow more sensitive detection of TDI emission. The protocol stated here is intended for screening dry polyurethane products such as carpet padding, upholstery foam materials, and polyurethane coated fabrics, as well as wet products such as polyurethane wood coatings, paints, caulks, and sealants. Other products not specifically named may be screened using this procedure, provided the test conditions are properly documented.

1.4 Hazards associated with the chemicals and procedures used in this protocol are stated in section 7. However, this protocol does not purport to address all of the potential safety issues resulting from its use. The user of this protocol is responsible for establishing safe operating conditions and procedures.
2. References
   2.1 Published documents that are the basis for this protocol are cited by means of
   Arabic numeral superscripts, and are listed in numerical order at the end of this document.

3. Terminology
   3.1 The terms used in this protocol are common in the field of chamber testing. The
   reader is referred to standard chamber test procedures\textsuperscript{4,6,8} for background on the terms used.

4. Significance and Use
   4.1 This screening protocol is specifically designed for evaluation of polyurethane
   products for the purposes of the CARB project cited above. The aim of this part of the project
   is to determine which consumer products, if any, may release significant quantities of TDI into
   the air in a residence. To date there is no substantial body of evidence to indicate significant
   TDI release from such products, but the potential toxicity of TDI is the motivating factor for
   this effort. The test results will allow CARB to inform the public whether indoor TDI
   emissions from polyurethanes are a concern, and which types of products produce the greatest
   emissions.

   4.2 The toxicity of the 2,4- and 2,6- TDI isomers may differ. As a result, the 2, 4-
   and 2, 6- TDI isomers will be determined separately by the NBPA method. Although
   commercial TDI mixtures used in producing polyurethanes are most commonly 80\% 2, 4-
   isomer, 20\% 2, 6- isomer (and less commonly 60\% 2, 4-, 40\% 2, 6-), there is evidence to
   suggest that in finished polyurethane products the 2, 6- TDI isomer predominates, because of
   its relatively lower reactivity. As a result the isomeric composition of the emitted TDI may
   not match that of the starting materials, and estimation of potential health effects may benefit
   from knowledge of the actual emitted isomeric composition.

   4.3 The screening procedure uses a single glass chamber of 9 liters (L) volume, held
   within a larger chamber which serves as a constant temperature enclosure. Initially, batches of
   similar products are tested together. Subsequent tests are then conducted on individual
   products if TDI is detected in the batch test. Product loading rates are exaggerated and
   temperature is elevated to enhance the detection of any TDI emission in the screening tests.

   4.4 TDI emission rates are estimated for those products that show a positive response
   in the screening tests. However, because of the exaggerated conditions used in the screening
   tests, the results must not be construed as actual in-home emission rates, nor used to
   extrapolate to in-home rates.

5. Apparatus
   5.1 Test Chamber: Screening tests are conducted in a glass chamber of 9 L volume,
   constructed by adding inlet and outlet tubing ports to a glass laboratory desiccator. The glass
   chamber is connected to an external clean air source by Teflon tubing, and the air exchange
   rate, temperature, and relative humidity of the chamber are controlled. The glass chamber is
   enclosed within a 0.44 m\textsuperscript{2} steel and glass chamber, which serves as a constant temperature
   enclosure, and which has a large door to allow ready access to the glass chamber. The inlet
and outlet tubing from the glass chamber passes through the outer chamber walls by means of bored-out bulkhead fittings; as a result the air flow through the glass chamber is exposed to only Teflon and glass surfaces. Two electrical heating elements are mounted inside the outer chamber, and are controlled by an external AC voltage source. The internal temperature of the outer chamber is monitored by means of a thermocouple located near the center of the chamber.

5.2 Internal Mixing: A 10 cm diameter muffin fan is suspended near the top of the outer chamber to promote mixing of air, and consequently uniform temperature, within the outer chamber.

5.3 Clean Air Supply: Air is supplied to the screening chamber from an Aadco pure air generation system, which removes water vapor, particulate matter, and gaseous contaminants from outdoor ambient air. The background TDI level from this source is zero. Air is provided from this system only to purge the chamber initially, and as needed to replace that withdrawn by the sampling methods, i.e., at most about 1.5 liters per minute during sampling. The purge flow of dry Aadco air is the same flow as used for zero/dilution air in a TDI calibration system, and is metered through a flow controller in that system. The air flow is then humidified by passage through a water bubbler at room temperature, to maintain about 20 percent relative humidity in the chamber at elevated temperature. All air exhausted from the chamber is vented into a laboratory fume hood.

5.4 Air Sampling Ports: The line for withdrawing sample air from the 9 L chamber is of 1/4" O.D. Teflon, about 2 feet long. Tests using a TDI permeation source with humidified dilution air have shown good results in transferring TDI at levels below 10 ppbv through such lengths of tubing.

5.5 Air Sampling and Analysis Methods: TDI in air within the screening chamber is determined by two distinct methods. Appendix A presents the justification for the use of these methods in this procedure. The two primary methods are as follows:

**Continuous Monitor** - A TLD-1 Toxic Gas Detector, manufactured by MDA Scientific, Inc., is used to provide a real-time continuous indication of chamber TDI levels. This monitor is based on a colorimetric detection system using reagent-impregnated paper tape cartridges. Exposure of the slowly moving tape to sample air produces a color change in the tape, the intensity of which is read automatically by a sensor and reported as the equivalent concentration of the target species. Selectivity of the monitor for isocyanates is dependent on use of the appropriate reagent tape. The monitor provides no distinction between the 2, 4- and 2, 6- TDI isomers. The monitor draws a sampling flow of about 0.5 L/min. Output of the monitor is in the form of a 4-20 mA signal, and a front panel display that reads to the nearest whole ppbv. The monitor can detect as little as 14 ug/m² (2 ppbv) of TDI; below that level the monitor reads 0 ppbv and puts out 4.00 mA. Above 2 ppbv the monitor responds linearly and sensitively to TDI, with a minimum detectable change of 0.02 mA, equivalent to about 0.08 ppbv. The TLD-1 is used in this study to give a yes/no indication of the presence of TDI.

**NBPA Method** - This method relies on reaction of diisocyanates with NBPA, to produce characteristic derivatives which are separated and quantified by high performance liquid chromatography (HPLC). Samples are collected by drawing 1 liter per minute of
chamber air for 20 minutes through an impinger containing NBPA in toluene solution. The collected diisocyanate derivatives are determined by reversed-phase HPLC with UV detection. This method separates and quantifies the 2, 4- and 2, 6- TDI isomers. This method has been used successfully in previous Battelle studies of TDI chemistry, and is the primary method to be used for quantitation of any TDI emissions in the screening tests. A 20 liter sample volume allows determination of as little as 0.7 ug/m³ (0.1 ppbv) of TDI.

6. Test Conditions

6.1 The screening chamber conditions are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>120 F (49 °C)</td>
</tr>
<tr>
<td>Air Exchange Rate</td>
<td>Static; then 10 hr⁻¹ during sampling, for dry products; 3 hr⁻¹ throughout testing, then 10 hr⁻¹ during sampling, for wet products.</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>Approx. 20 %</td>
</tr>
</tbody>
</table>

Consistent test temperature is maintained by enclosure of the 9 L chamber within the outer steel and glass chamber, which is equipped with internal heating elements and a fan. Air exchange rate is determined by the flow of air needed to make up for that withdrawn in sampling. For most of the duration of each dry product screening test, the chamber will be static, i.e., air flow will be zero. At the end of the test, the chamber air will be sampled with both the NBPA impinger and the TLD-1 monitor simultaneously, resulting in a total air exchange rate of about 10 hr⁻¹ during sampling. In contrast, the TLD-1 is operated throughout each screening test on wet products, resulting in an air exchange of 3 hr⁻¹. The input air is nearly saturated with water vapor at room temperature, resulting in a relative humidity of about 20 % at the elevated chamber temperature.

6.2 The chamber loading (i.e., m²/m³) of products undergoing screening is exaggerated above that typical in a home. Table 1 presents the loading rates to be used in screening various types of products, and Appendix B presents the rationale behind these rates.

7. Hazards

7.1 Normal care is required in laboratory procedures with the NBPA method. Avoid inhalation or skin exposure of toluene or of the NBPA-toluene reagent. TDI is highly toxic; use with care, and vent any gas streams known or suspected to contain TDI vapors into a hood for disposal. Wet products being tested, such as coatings and sealants, should be used as directed on the product's label.

8. Sample Storage

8.1 Sample storage prior to testing is intended to prevent contamination of sample materials by one another or by the surroundings, and to prevent decay of any TDI emissions during storage. Samples are subjected to screening no more than two months after receipt at
TDI Screening Protocol
Revision Date: April 29, 1996

Battelle. Prior to testing, samples are held in a secure, well-ventilated area, under normal conditions of temperature and relative humidity (i.e., 73 +/- 5 F; 50 +/- 5 % RH).

8.2 All samples obtained in packaged form are stored in their original packaging until tested. Samples not ordinarily obtained in packaged form are shipped to Battelle wrapped in plastic film. Such samples are removed from the film wrapping a few days before testing, at which time samples are cut into appropriate size pieces for testing.

8.3 Sample materials are shipped to Battelle in quantities sufficient for both initial screening of product groups and final screening of individual materials.

9. Test Procedure: Dry Products

9.1 Chamber Background: Before each screening test purge the 9 L glass chamber with sufficient humidified Aaego air to replace the chamber volume at least 5 times. Clean the chamber internal surfaces with water after each test, or as needed to maintain a TDI background that is non-detectable by the TLD-1 monitor. Close the glass chamber, allow the temperature to stabilize, and sample the chamber air with the TLD-1 and with the NBPA method; the absence of response on the TLD-1 is indicative of an acceptable chamber background. During background sampling provide humidified Aaego air to the chamber as needed to replace the air withdrawn in sampling.

9.2 Loading the Chambers: After completion of the chamber background sampling, enclose test samples in the glass chamber at the loading rates specified in Table 1, and close the outer chamber door. Place test samples in such a manner that they do not overlay one another. Turn off any air flow into the chamber and seal inlet and outlet ports.

9.3 Test Period: Maintain the test samples in the chamber at test conditions for at least four (4) hours.

9.4 Chamber Conditions: Record the chamber temperature at intervals during the test, and adjust as necessary to maintain 49 (+/- 2 °C).

9.5 TDI Sampling: At the conclusion of the test, sample the chamber air for 20 minutes with both the TLD-1 and the NBPA methods. During sampling provide humidified Aaego air to the chamber as needed to replace the air withdrawn in sampling. Record the volume and duration of air flow supplied to the chamber during sampling.

9.6 Emptying the Chambers: At the completion of the test, if the TLD-1 monitor showed no indication of TDI, open the outer chamber door and remove the samples from the 9 L glass chamber. If the TLD-1 monitor indicated the presence of TDI, purge the glass chamber with several volumes of Aaego air before opening the door, venting the chamber contents into a laboratory fume hood.

9.7 TDI Analysis by NBPA: Analyze the impinger solutions by IIPLC according to the procedures used in previous studies. Quantify the TDI concentrations in the impinger solutions by HPLC analysis of TDI standards prepared in the same reagent mixture.

9.8 Initial and Final Screening: Conduct initial screening tests on groups of 3 to 6 similar products. If a group of products is found to emit TDI (see section 11 for the definition of a positive screening result), repeat steps 9.1 - 9.6 as necessary to conduct screening on smaller groups of that type, or on individual products, to identify the emitting products.
TDI Screening Protocol
Revision Date: April 29, 1996

Maintain the same product loading rate in testing of individual products, or of smaller groups of products, as was used in the original group test (see Table 1).

10. Test Procedure: Wet Products

10.1 Chamber Background: Determine the chamber background and load the chamber as described in sections 9.1 and 9.2.

10.2 TDI Sampling: Sample the chamber air continuously with the TLD-1 monitor from the time the samples are placed in the chamber, providing humidified clean air to make up for sample air withdrawn from the chamber. Sampling with the NBPA method may be initiated at any time after a positive response is indicated on the TLD-1. If the TLD-1 shows no indication of TDI after the samples have been in the chamber for 4 hours, sample the chamber air with the NBPA method, then end the test. Record chamber and sampling conditions as described in sections 9.4 and 9.5.

10.3 Emptying the Chambers: Empty the chamber, perform TDI analysis, and conduct initial and final screening as described in sections 9.6 through 9.8.

11. Calculations

11.1 General: A positive result in the screening test is defined as a detectable increase above the respective chamber background level with either the TLD-1 monitor or the NBPA method. In the case of disagreement between the two methods as to the detection of a positive result, the NBPA result will be adopted, because that method is both more sensitive and more specific for TDI. The minimum detectable increase above zero air background on the TLD-1 is 14 ug/m² (2 ppbv). The minimum detectable level for the NBPA method has been shown in laboratory tests to be about 0.7 ug/m² (0.1 ppbv).

11.2 TLD-1 Readings: The response of the TLD-1 is recorded as a 4-20 mA signal. Calculation of ppbv levels is as follows:

\[ \text{TDI (ppbv)} = (\text{mA Reading} - 4.0 \text{ mA}) \times 3.752 \]

where the factor of 3.752 is a scale factor built into the monitor. Conversion of ppbv TDI to ug/m² units is done using the conversion 1 ppbv TDI = 7.2 ug/m³.

11.3 NBPA Results: Calculate the chamber TDI concentration determined by the NBPA method as follows:

\[ \text{TDI (ug/m³)} = \frac{\text{TDI (ug/ml NBPA)} \times \text{Volume NBPA (ml)}}{\text{Sampled Air Volume (m³)}} \]

11.4 Dry Product Emission Rates: For dry products showing TDI emissions, the approximate surface emission rate is estimated from the TDI concentration determined at the end of the test, with appropriate correction for the loss of some TDI to the chamber walls. Tests with ppbv levels of TDI indicated a loss rate of about 0.7 hr⁻¹ in the 9 L chamber (see section 14.3). With this loss rate, at the end of a 4-hour static test, only about one-third as...
TDI Screening Protocol
Revision Date: April 29, 1996

much TDI would be present in the chamber air as in the absence of a surface sink. Thus the
emission rate from dry products was calculated as follows:

\[ ER \ (\text{ug/m}^3/\text{hr}) = \left[ \text{Conc. (ug/m}^3\right) \times \text{Vol. (m}^3\right) \times \text{CF}\right]/\left[\text{time (hr) \times Area (m}^2\right] \]

where
\[ ER \]  = the estimated average surface emission rate of the product or group of
products;
\[ \text{Conc.} \]  = the measured TDI concentration in the chamber at the end of the test;
\[ \text{Vol} \]  = the chamber volume (0.009 m\(^3\));
\[ \text{CF} \]  = correction factor to account for surface loss of TDI; = 3 for a 4-hour test;
\[ \text{time} \]  = the time in hours from placing the sample in the chamber to the start of the
concentration measurement;
\[ \text{Area} \]  = the total exposed surface area of the product or products.

In addition, when applying the equation above to the NBPA results, an additional
correction factor of 1.5 must be used, to account for the fact that when sampling
simultaneously with the two methods, only two-thirds of the sample flow goes to the NBPA
impinger.

11.5 Wet Product Emission Rates: If TDI is detected by the TLD-1 monitor during
testing of a wet product, without simultaneous NBPA sampling, the product emission rate is
estimated as:

\[ ER \ (\text{ug/m}^3/\text{hr}) = \left[ \text{Conc. (ug/m}^3\right) \times N \ (\text{hr}^{-1}) \times \text{CF}\right]/\left[L \ (\text{m}^3/\text{m}^3) \right] \]

where \( ER \) and \( \text{Conc.} \) are as defined above, and
\[ N \]  = air exchange rate (i.e., 3 hr\(^{-1}\));
\[ L \]  = product loading in chamber, i.e., the exposed surface area of product divided by
the chamber volume;
\[ \text{CF} \]  = correction factor of 1.25 to account for loss of TDI in the chamber.

If TDI is detected by the NBPA approach during testing of a wet product, the same
equation is used except that \( N \) has the value of 10 hr\(^{-1}\), and as in section 11.4 an additional
correction factor of 1.5 must be used.

11.6 Purpose: The \( ER \) values calculated as described in 11.4 and 11.5 are for
approximate comparison of TDI emission strengths of different products under screening
conditions, and are not to be construed as actual in-home emission rates.
12. Sensitivity of Screening

12.1 General: An important issue is the degree to which the screening tests accurately discern the likelihood of TDI emissions from the products under realistic in-home conditions. Three factors are important: 1) the detectability of any TDI emissions in the screening tests, 2) the relation of emissions under screening conditions to those under realistic in-home conditions, and 3) the impact of in-home TDI emissions on in-home TDI concentrations and health risks. The following sections discuss those factors.

12.2 Detectability of Dry Product Emissions: Assuming a detection limit of the TLD-1 monitor of 2 ppbv (14 ug/m$^3$) of TDI, and assuming that a total area of 0.124 m$^2$ of a dry product is exposed in the chamber (see Table 1) under static conditions for 4 hours, then a negative screening result implies a surface TDI emission rate less than

\[
ER = \frac{[14 \text{ ug/m}^3 \times 0.009 \text{ m}^3 \times 3]}{[4 \text{ hr} \times 0.124 \text{ m}^2]} \\
= 0.76 \text{ ug/m}^2/\text{hr of TDI}
\]

The detection limit of the NBPA method is lower than that of the TLD-1. Taking a reasonable detection limit value of 0.1 ppbv (0.7 ug/m$^3$), doubling it to account for the fact that a 20 L sample size is needed though the chamber is only 9 L, and applying the appropriate correction factors, a negative response on the NBPA method indicates a surface TDI emission rate of less than about 0.11 ug/m$^2$/hr.

12.3 Detectability of Wet Product Emissions: In tests of wet products, a detection limit of 0.7 ug/m$^3$ for the NBPA method equates to a minimum detectable TDI emission rate of 1.3 ug/m$^2$/hr, based on an N value of 10 hr$^{-1}$ and an L value of 6.93 (i.e., 0.0624 m$^2$ in a 0.009 m$^3$ chamber, Table 1). The corresponding calculation for the TLD-1 in the absence of NBPA sampling (i.e., with an N value of 3 hr$^{-1}$) gives a minimum detectable rate of 7.6 ug/m$^2$/hr.

12.4 Relation to Realistic Conditions: The screening tests are conducted at elevated temperature relative to in-home conditions. Vapor pressure data for TDI indicate that increasing the temperature from about 20°C to about 50°C (i.e., to about 120 °F) increases the TDI vapor pressure by about a factor of ten.$^6$ As a result, we can assume a factor of 10 greater emission rate at screening conditions relative to that at in-home conditions. Thus for dry products a negative screening result from the TLD-1 suggests an in-home emission rate of less than 0.076 ug/m$^2$/hr, and a negative screening result in the NBPA analysis suggests an in-home rate less than 0.011 ug/m$^2$/hr. For wet products the corresponding minimum detectable rates for the TLD-1 and NBPA are about 0.76 and about 0.13 ug/m$^2$/hr, respectively.

12.5 Health Risk Comparison: Assuming an in-home air exchange rate of 0.5 per hour, and a product loading of 0.3 m$^2$/m$^3$ (typical of carpet padding, the most widely used dry polyurethane product), the realistic detectable emission rates estimated in section 12.4 are calculated to give steady state TDI concentrations in the home of about 0.046 ug/m$^3$ and 0.007 ug/m$^3$, respectively, from a dry product.

Assuming the same in-home air exchange rate, and a product loading of 0.1 m$^2$/m$^3$ (representative of a polyurethane wood coating, a common wet product), the detectable
TDI Screening Protocol
Revision Date: April 29, 1996

emission rates estimated in section 12.4 give steady state in-home TDI concentrations of about 0.15 ug/m$^3$ and 0.026 ug/m$^3$, respectively, from a wet product.

For comparison to these results, the TDI concentrations that result in lifetime cancer risks of $1 \times 10^{-6}$ and $1 \times 10^{-5}$ are about 0.09 ug/m$^3$ and 0.9 ug/m$^3$, respectively.

13. Reporting
13.1 Report the screening test results in a summary final report to CARB. That report must include information on the samples tested, the test procedures, the analytical methods, and the test results.

13.2 Samples Tested: To the extent possible, describe the nature and origin of the tested samples. Include the date and place of purchase, the manufacturer, product type and dimensions, product lot or production number, and any information on the chemical composition of the product.

13.3 Test Procedures: Describe the shipping and storage of the samples. Document the chamber characteristics and actual test conditions, including particularly temperature, background TDI level, and product loading rates.

13.4 Analytical Methods: Describe the analytical procedures, including any QA results that indicate precision, accuracy, and detection limits. Discuss any observations on the relative performance or usefulness of the methods employed.

13.5 Test Results: Report the screening test results for each group of products or individual products. Report both the qualitative indications of TDI emissions (i.e., presence or absence of TDI) and the quantitative indications, from both the TLD-1 and NBPA methods. Compare the TDI concentrations determined simultaneously by the two methods, and calculate the TDI emission rate for any product or group of products exhibiting a positive screening result. Report the isomeric composition of TDI determined by the NBPA method. Also report any data resulting from any alternative method used.

13.6 Discuss the results for the various product types relative to their importance as indoor TDI sources, and recommend which products should undergo further testing under more realistic test conditions.

14. Precision and Bias
14.1 The TLD-1 monitor compared well with the NBPA method in simultaneous measurements in previous work. A comparison of TLD-1 and NBPA results was made over a range of TDI concentrations of 10 to 180 ppbv, based on 32 samples taken during 6 different chamber studies.\textsuperscript{3-5} In those tests, varying levels of humidity, volatile organic compounds, ammonia, ammonium sulphate particles, light intensity, and other potential reactants were present. A linear regression to the data exhibited the form

$$TDI_{TLD-1} = TDI_{NBPA} \times 1.053 (\pm 0.046) + 3.88 (\pm 10.87) \text{ ppbv},$$
TDI Screening Protocol
Revision Date: April 29, 1996

where the error bars are 95 percent confidence limits, with an $R^2$ value of 0.947. Furthermore, TDI loss rates determined by the two methods in the six chamber experiments agreed within 7.5 percent.

14.2 Tests of both the TLD-1 monitor and the NBPA method were conducted prior to the screening tests described here, using a permeation tube source of 2,4-TDI. Tests with the TLD-1 demonstrated that TDI is readily transported through a few feet of Teflon tubing, and through the glass test chamber, at levels of 5 ppbv or less. TDI concentrations stabilized within a few minutes after switching the source output between zero air and a TDI mixture. The detection limit of the NBPA method was established by sampling of zero air and of TDI at levels below 5 ppbv. Good agreement was observed between the TLD-1 and NBPA methods in simultaneous sampling of the permeation tube output. The precision and accuracy of TDI measurements are both estimated to be 20 percent, for both the TLD-1 and NBPA methods.

14.3 The loss rate of TDI in the glass chamber was determined by drawing known ppbv concentrations of TDI through the chamber with the TLD-1 monitor, and comparing upstream and downstream TDI concentrations. At concentrations of 4.2 to 6.8 ppbv an average recovery of 80 percent was found. Based on the 20-minute residence time of air in the chamber in these tests, a TDI loss rate of 0.7 per hour was calculated. Corrections for this loss rate have been applied in calculating the product emission rates and screening sensitivities in sections 11 and 12 of this protocol.

15. References


D-10
Table 1. Product Loading Rates for TDI Screening of Product Groups and Individual Products

<table>
<thead>
<tr>
<th>Category/Product</th>
<th>Loading Rate (m²/m³)</th>
<th>Required Surface Area (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carpet Padding (Group)</td>
<td>13.9</td>
<td>0.124&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Carpet Padding (Individual)</td>
<td>13.9</td>
<td>0.124&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Foam Cushions (Group)</td>
<td>13.9</td>
<td>0.124&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Foam Cushions (Individual)</td>
<td>13.9</td>
<td>0.124&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Polyurethane Coatings (Group)</td>
<td>6.9</td>
<td>0.0624&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Polyurethane Coatings (Individual)</td>
<td>6.9</td>
<td>0.0624&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Polyurethane Coated Fabrics (Group)</td>
<td>11.6</td>
<td>0.104&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>&quot; &quot; (Individual)</td>
<td>11.6</td>
<td>0.104&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Concrete Sealer (Group)</td>
<td>5.8</td>
<td>0.052&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Concrete Sealer (Individual)</td>
<td>5.8</td>
<td>0.052&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mastic Construction Sealants (Group)</td>
<td>3.5</td>
<td>0.031&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>&quot; &quot; (Individual)</td>
<td>3.5</td>
<td>0.031&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> This surface area will be achieved by using one 10.2 cm x 10.2 cm (4 in x 4 in) double-sided piece of each of six different products, for group screening; the same surface area will be achieved by using six 10.2 cm x 10.2 cm double-sided pieces of the test product, for individual screening.

<sup>b</sup> This surface area will be achieved by using a separate 10.2 cm x 10.2 cm (4 in x 4 in) piece of appropriate substrate material (e.g., wood, metal) for each of six products, for group testing. Each product will be applied to one side of the substrate. The same surface area will be achieved by using six 10.2 cm x 10.2 cm pieces of appropriate substrate material (e.g., wood, metal) for application of the test product, for individual testing.

<sup>c</sup> This surface area will be achieved by using one 10.2 cm x 10.2 cm (4 in x 4 in) double-sided piece of each of five products, in group testing, or five 10.2 cm x 10.2 cm double-sided pieces of one product, in individual testing.

<sup>d</sup> This surface area will be achieved by using a 10.2 cm x 10.2 cm single-sided area of concrete substrate for application of each of five products, for group testing. The same surface area will be achieved by using five pieces of the same size for application of the test product, for individual testing.

<sup>e</sup> This surface area will be achieved by using a separate 10.2 cm x 10.2 cm (4 in x 4 in) wood substrate for each of three products, for group testing. Each product will be applied to one side of the substrate. The same surface area will result from using three such pieces for individual testing.
APPENDIX A
SELECTION OF TDI SCREENING METHODS

Background
In preparation for selecting candidate TDI screening methods for the CARB project, a
literature search was carried out which revealed that most researchers currently use one of
three derivatization procedures in order to collect and speciate TDI isomers. All three
procedures make use of high performance liquid chromatography (HPLC) for compound
separation with either ultraviolet (UV) or fluorescence detection.

N-(4-nitrobenzyl)-N-n-propylamine nitreagent (NBPA) -
Dunlap et al (1976) were the first to combine the NBPA nitreagent
derivatization approach with HPLC to provide a method that is in widespread
use today. They used a UV detector to sense the aromatic ring structure present
in the derivatives. The method has held up well over the years and has good
sensitivity and specificity and is free of interferences. An early concern was
that excess nitreagent eluting during chromatography may cause gradual
deterioration of the analytical column. Bagon and Purnel (1980) and more
recently Rando et al (1984) added acetic anhydride to acetylate excess
nitreagent and therefore eliminate this concern. Rosenberg (1984) used
NBPA reagent both for impinger sampling and for coating glass fiber filters. In
all of the above studies, reported TDI detection limits generally ranged from 0.1
to 0.2 ppbv for a 20-liter air sample.

1-(2-pyridyl)piperazine reagent (1-2PP) -
Hardy and Walker (1979) were the first to introduce the 1-2PP reagent for
derivatizing isocyanates for HPLC analysis. The reagent was thought to be
more stable toward air oxidation than the NBPA reagent. However, the
researchers using NBPA reagent have not reported NBPA oxidation to be a
problem, but do recommend preparation of fresh NBPA solutions every 4-5
weeks. The OSHA Method No.42 (1989) also uses the derivatizing reagent
1-2PP coated onto glass fiber filters. The method has a reported quantitation level
of 0.3 ppbv for a 15 liter air sample. The 1-2PP-based urea derivatives have
been reported to have higher molar absorptivities than the NBPA urea
derivatives and therefore should have somewhat higher signal response on the
HPLC. Hodgson et al (1993) have recently examined this aspect, and also
incorporated fluorescence detection to further lower the detection limit of TDI-
urea derivatives. By improving chromatography and sampling conditions, these
researchers were able to achieve a ten fold improvement over the OSHA
quantitation level (i.e., to 0.03 ppbv).
TDI Screening Protocol
Revision Date: April 29, 1996

9-(N-methylaminomethyl)-anthracene reagent (MAMA) - Although not frequently used, several researchers have indicated that the MAMA reagent also works well for TDI derivatization (Sango et al 1980, Persson et al 1993). Persson et al (1993) reported measuring 0.06 to 0.6 ppbv of TDI using this reagent with HPLC/UV detection. However, the air sampling volume was not reported.

The above studies indicate that all three derivatization approaches work reasonably well for speciating and analyzing the TDI isomers. The reported quantitation levels are within a factor of ~3.

Several on-line monitoring instruments have also been used routinely for isocyanate determinations in industrial workplaces. The MDA Company (Lincolnshire, IL) has developed both area monitors (Models 7000, 7100, TLD-1) and personal monitors (Models 4000, IsoLogger). These units use a specially formulated tape that is highly specific and changes color in direct proportion to the amount of TDI vapor. Depending upon the instrument model, the time required to respond to concentration transients ranges from several minutes to approximately 15 seconds. GMD Company had also produced similar instruments in the mid-1980's. An ion mobility spectrometer (Graseby Company) has also been reported to measure trace levels of TDI vapor (Broksenshire et al, 1990).

Levine et al. (1995) have reviewed all of the above measurement approaches and have compared the advantages and disadvantages of each. That review includes discussion of other measurement issues, such as the use of inappropriate types of inlet lines, instrument non-linearity, methods for determining levels of detection and quantitation, etc.

Selection of Methods for CARB Project
Battelle staff have selected two TDI screening methods. The first method is a commercial colorimetric monitoring instrument from MDA. The instrument (TLD-1) makes use of a specially formulated tape that changes color in the presence of the toluene diisocyanate isomers. Continuous monitoring of total TDI isomers is achieved at ppbv levels. The second method makes use of a midget impinger filled with a solution containing N-(4-nitrobenzyl)-N-n-propylamine (NBPA) in toluene. The derivatized TDI isomers are then separated and analyzed using high performance liquid chromatography (HPLC). Detection of the individual isomers at sub-ppbv levels is achieved with this approach. Justification for the use of these two methods for this project follows.

Continuous TDI monitor

Battelle staff have extensive experience with the continuous TDI monitor (Model 7100) that is currently produced as the TLD-1 by MDA Scientific. Our past studies with the Model 7100 have shown that this type of instrument provides accurate, selective and relatively rapid
TDI Screening Protocol
Revision Date: April 29, 1996

indication of the presence of TDI at concentrations in the low ppbv range (Holdren et al. 1983, 1984). The TDI monitor's response compared well with calculated amounts of TDI that were injected into Battelle's 17.3 m³ environmental chamber. The TDI monitor also compared well with the NBPA impinger /HPLC method during chamber studies of the atmospheric fate of TDI. For example, Figure 1 shows a comparison of results from the continuous instrument and the impinger/HPLC method obtained during 6 different chamber studies (Holdren et al. 1985). In these tests, varying levels of humidity, VOCs, ammonia, ammonium sulphate particles, light intensity and other potential reactants were present. As the figure indicates, the agreement between methods was very good. The 1-to-1 line (solid) is shown, along with a linear regression to the data (dashed line). The equation has the form:

\[
TDI_{\text{continuous}} = TDI_{\text{NBPA}} * 1.053 (+/- .046) + 3.88 (+/-10.87) \text{ ppbv}
\]

where the error bars are 95 percent confidence limits, with an \( R^2 \) value of 0.947. The instrument's measuring range is from 1 to 200 ppbv (DL = 1 ppbv using a sample averaging time of 2 minutes).

A key reason for use of the TDI monitor in this study is its unique real-time capability, which will allow direct observation of the course of the screening tests, and will assure the safety of study personnel by directly indicating the chamber TDI level.

**NBPA method**

The derivatization of TDI with N-(4-nitrobenzyl)-N-n-propylamine (NBPA) in toluene solution, followed by reversed phase HPLC and UV detection was also extensively used by Battelle staff in the above referenced studies. During those studies, collection of a 20-liter air sample allowed the detection of 2 ppbv of TDI in the test chamber. Recent improvements in Battelle's HPLC equipment allow us to achieve a detection limit of 0.1 ppbv when using the 20-liter collection volume, with detection by UV absorption at 215 nm wavelength. A recent chromatogram showing the resolution of the 2,4- and 2,6-TDI derivatives is shown in Figure 2.

A limitation of the NBPA impinger method noted by Levine et al. (1995) is the relative inefficiency of aerosol collection common to all impinger methods. However, this limitation is of no concern for the present study, because TDI is known to exist virtually entirely in the vapor phase at normal conditions (Levine et al., 1995). As noted above, the 1-2PP method with fluorescence detection (Hodgson et al., 1993) does potentially offer a 3-fold improvement in TDI detection, relative to the NBPA method. However, as described in section 12 of this protocol, the sensitivity obtained with the NBPA method is ample for this program. Furthermore, the method described by Hodgson et al. (1993) requires coating of filters with reagent prior to sampling, followed by extraction of the filters after sampling. The extra effort needed for these steps may be important in obtaining reliable data in the field, but is likely to
TDI Screening Protocol
Revision Date: April 29, 1996

be unnecessary in this study, conducted entirely in a laboratory setting. As a result, and in light of the extensive experience of Battelle staff with the NBPA method, we believe that use of the NBPA method is preferable to changing over to the 1-2PP /fluorescence method.

References

APPENDIX B: RATIONALE FOR LOADING RATES IN TDI SCREENING

The loading rates shown in Table 1 were chosen based on the likely emission rates, in-home loadings, and manner of use of the target products, as well as on the criteria of detectability of the screening results, comparability of the various screening tests, and product sample size needed. Because the present tests are for screening purposes only, realism in testing was sacrificed in order to achieve detectability and comparability of test results, and to select reasonably attainable sample sizes. Also, because initial screening of products in groups is planned, the number of products of each type was considered. As described in the product selection for this study,\(^{(1)}\) it is planned that a total of 12 carpet padding samples, 12 foam cushion samples, 12 polyurethane coatings, 5 polyurethane coated fabrics, 5 concrete sealers, and 3 mastic construction sealants will be tested. This appendix briefly summarizes the reasons for the stated product loadings.

All of the product loading rates stated in Table 1 exceed the likely in-home rates by a large factor, to promote detection of any TDI emissions during screening. The loading rates shown for carpet padding, cushions, and coatings reflect the testing of these products in groups of 6. The indicated loadings are readily achieved in the 9 L chamber using a small surface area for each product, yet the total loading can also be readily achieved for an individual product. These three categories represent the bulk of polyurethane production; comparability among the tests for these product types is assured by using comparable product loadings.

For polyurethane coated fabrics, the loading indicated was obtained by using the same surface area per product in group testing, but with the recognition that only 5 samples are to be tested. The loading is close that of the other categories, to assure adequate comparability.

For the category of concrete sealers, the nature of the substrate (concrete) was important. As a wet product, the concrete sealers are among the most likely sources of TDI within the products to be tested. Application of concrete sealer to give the indicated loading rate should produce a detectable signal if TDI is emitted. Furthermore, use of a small concrete substrate will protect the glass chamber and make handling the substrate relatively simple.

Comparability of test results for mastic sealants to those of concrete sealants was considered important. As a result, the same substrate area is planned. However, for mastic sealants there will be only 3 products tested, rather than 5.

\(^{(1)}\) Selection of Products for Chamber Testing, report prepared for the California Air Resources Board, Project No. 93-315, by Battelle, Columbus, Ohio, March 1995.
APPENDIX E

QUALITY ASSURANCE PROJECT PLAN
FOR
CHAMBER TESTING OF FORMALDEHYDE EMISSIONS
FROM INDOOR RESIDENTIAL SOURCES

The document shown in this Appendix was prepared during the course of Research Project 93-315, and served as the basis for a portion of the project. However, the main body of this report should be consulted as the most complete and final presentation of the study activities and results.
QUALITY ASSURANCE PROJECT PLAN
FOR
CHAMBER TESTING OF FORMALDEHYDE EMISSIONS FROM
INDOOR RESIDENTIAL SOURCES

California Air Resources Board Project 93-315

prepared by
Battelle
505 King Avenue
Columbus, Ohio 43201-2693

Revision Date: June 7, 1995

1. Introduction

1.1 This document is the Quality Assurance Project Plan (QAPP) for the California Air Resources Board (CARB) project noted above. This QAPP specifically addresses chamber tests performed to determine the formaldehyde (HCHO) emission rates of diverse products used in California residences. The test results will allow CARB to inform the public as to what are the most important indoor formaldehyde sources, with the goal of reducing the public's exposure to formaldehyde indoors.

1.2 This QAPP applies to the range of products identified as likely to be found in California homes, in Battelle's product selection report for this study.\(^1\) The products to be tested include dry materials such as wood products, fabrics, insulation, decorative laminates, and paper goods, as well as wet products such as paints, coatings, cosmetics, and wallpaper. Written protocols exist for performance of chamber testing on both dry and wet products.\(^2,3\) This QAPP states the quality assurance procedures to be used in performing the chamber emission tests, acquiring the test data, and evaluating the collected data.

2. Data Quality Objectives

2.1 The Data Quality Objectives (DQO's) for the chamber testing include aspects of the samples to be tested, the chamber test conditions, and the chemical measurements made. Table 1 lists the DQO's for the pertinent parameters, in terms of the precision, accuracy, and completeness to be achieved. In that table, precision and accuracy are quantified in terms of the standard deviation of the indicated parameter. The DQO's for precision and accuracy apply regardless of the type of product being tested, however the DQO's for data completeness in testing of wet products differ slightly from those for testing of dry products. Section 7 of this document describes the procedures for assessing precision and accuracy.

2.2 The DQO's for data completeness in Table 1 indicate the minimum percentage of all tests in which the indicated parameters must be documented. This does not mean that all the parameters listed must be recorded continuously at least 90 percent of the time during all tests. Rather, the data completeness DQO's indicate that the parameters shown must be recorded at the time of chemical sampling, with sufficient time resolution to document that
Quality Assurance Project Plan
Revision: June 7, 1995

Table 1. Data Quality Objectives for Chamber Testing

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Precision</th>
<th>Accuracy</th>
<th>Dry Prods.</th>
<th>Wet Prods.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>+/- 1 C</td>
<td>+/- 0.5 C</td>
<td>&gt; 90%</td>
<td>&gt; 90%</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>+/- 5% RH</td>
<td>+/- 5% RH</td>
<td>&gt; 90%</td>
<td>&gt; 90%</td>
</tr>
<tr>
<td>Air Exchange Rate&lt;sup&gt;b&lt;/sup&gt;</td>
<td>+/- 2%</td>
<td>+/- 2%</td>
<td>&gt; 90%</td>
<td>&gt; 90%</td>
</tr>
<tr>
<td>Sample Area&lt;sup&gt;c&lt;/sup&gt;</td>
<td>+/- 1%</td>
<td>+/- 1%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>HCHO Concentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Real-time monitor</td>
<td>+/- 5%</td>
<td>+/- 10%</td>
<td>&gt; 90%&lt;sup&gt;d&lt;/sup&gt;</td>
<td>100%&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>DNPH sampling</td>
<td>+/- 5%</td>
<td>+/- 10%</td>
<td>100%&lt;sup&gt;e&lt;/sup&gt;</td>
<td>&gt; 90%</td>
</tr>
</tbody>
</table>

(a): Dry prods. = wood products, decorative laminates, fabrics, insulation, paper products; Wet prods. = paints, coatings, cosmetics, wallpaper.
(b): Refers to total air exchange rate due to sum of dry and humidified air flows into the chamber.
(c): Surface area of material, excluding edges, or of substrate, in the case of wet products applied in the chamber.
(d): Real-time monitor generally required for all tests, but in some specific cases test may be conducted without real-time data; see reference 2.
(e): Critical measurement; absence of data invalidates test.

The parameters are within the indicated precision ranges. Temperature and relative humidity are in fact monitored continuously in the chamber tests; the DQO’s simply indicate that data must be recorded frequently enough while chemical sampling is being done to document that the parameters are within the indicated precision ranges. The frequency of recording required to establish the test parameters depends on the stability of the chamber parameters. Experience with the test chambers indicates that values recorded at least every half hour during chemical sampling should be sufficient to define the test parameters.

2.3 The DQO’s shown in Table 1 for data completeness are 100 percent for real-time formaldehyde monitoring<sup>4</sup> in testing of wet products, and for DNPH<sup>2</sup> measurements in testing of dry products. These 100 percent DQO’s are set because of the critical nature of these chemical measurements. Without continuous formaldehyde measurements during testing of a wet product, the test is meaningless, regardless of the precision and accuracy of the other test parameters. The same applies to the DNPH sampling conducted for quantitation in the dry product tests. As a result, any chamber test for which the critical chemical measurement is not achieved will be invalidated and repeated.

3. Calibration
3.1 DNPH Method - The 2,4-dinitrophenylhydrazine (DNPH) method will be employed according to the guidelines of EPA Compendium Method TO-5.<sup>5</sup> The DNPH method is calibrated by preparation of aldehyde/DNPH derivatives from the pure starting
materials, and serial dilution of those derivatives to known levels comparable to those in the test samples. This procedure will be followed for formaldehyde and for the additional carbonyl compounds of interest in this study (acetaldehyde, propionaldehyde, methyl ethyl ketone, and methyl iso-butyl ketone). A single standard containing all five of the target carbonyls will be used. Experience in many previous studies has shown that dilute standards prepared in this way are stable over periods of several months, with the formaldehyde derivative the least stable of the three target derivatives. As a result, dilute standards containing all five target compound derivatives will be prepared at the time of initial sample analyses, and used until the peak area of the formaldehyde derivative in the standards declines by 10 percent from its initial value. A control chart of standard analyses will be maintained to track the peak areas over time. Once a 10 percent drop in formaldehyde peak area has been observed, a new standard solution will be prepared.

Dilute standards, typically of 2 ug/ml concentration, will be analyzed by HPLC as described in Method TO-5 on every day that a batch of test samples is analyzed. Standards will be intermingled with test samples, to assure comparability of results. Blank samples, i.e., samples of chamber background air obtained prior to each chamber test, will be analyzed in the same batch as the corresponding test samples. Blank chamber results will be subtracted from the corresponding test and calibration results before calculation of test concentrations.

3.2 Real-Time Formaldehyde Method - The real-time monitor is calibrated with solutions of formaldehyde in 0.1 N sulfuric acid, which are substituted for the 0.1 N sulfuric acid scrubber solution normally used in the instrument. Under typical operating conditions, a solution of 1 x 10^{-6} M formaldehyde is equivalent to sampling of 10 ppbv formaldehyde in air. In this study, solutions ranging from 1 x 10^{-6} M to 1 x 10^{-4} M formaldehyde (equivalent to roughly 10 ppbv to 1 ppmv) will be prepared as necessary by serial dilution of standard formalin solution (37 percent formaldehyde by weight; 13.3 M formaldehyde; Baker reagent grade or equivalent). Experience in field studies indicates that prepared standards in this concentration range are stable within about 5 percent over periods of a few days at room temperature. For this study, fresh standards will be prepared every third test day or when a 5 percent loss of response is observed, and standards will be run on every test day. The dilute standards will be prepared by dilution of stock solutions of about 1 x 10^{-3} M formaldehyde. That stock solution will be prepared fresh weekly.

The background signal of the real-time monitor will be determined on each test day by sampling of high purity air, either from a commercial cylinder, or from the air source supplying the test chambers. The background signal will be zeroed out automatically in the real-time monitor’s electronics. The chamber background formaldehyde level will also be determined using both the monitor and the DNPH method on each test day, prior to introduction of a test sample into the chamber.

4. Training and Maintenance

4.1 Operator Training - All chamber tests will be conducted by Battelle staff fully familiar with the test protocols and with this QAPP, and experienced in the operation of the chambers and test equipment. Following approval of the test protocols and QAPP by
Quality Assurance Project Plan
Revision: June 7, 1995

CARB staff, copies of the final versions of those documents will be provided to all project staff. Should any revision of the test protocols be necessary (e.g., as a result of experience in conducting the tests), CARB approval will first be obtained and then all project staff will be notified of the revisions.

Staff will have separate and specific assignments that assure proper focus on key aspects of the project. For example, one staff member will have primary responsibility for sample receipt and custody, and for recording and documenting test results. Another staff member will be responsible for maintaining the chambers and conducting the actual chamber tests. A third staff member will conduct the formaldehyde measurements both by the real-time and DNPH methods. These methods are standard in Battelle's laboratory, and performance of both methods by a single staff member is readily achieved. All tests will be supervised and the data reviewed by the Principal Investigator (Dr. Thomas Kelly) who is responsible for the technical aspects of this study. The project staff are all capable of filling multiple roles on the project, and will back one another up as needed. Furthermore, one additional part-time staff member is available as backup for any of the various activities.

4.2 Maintenance - The test chambers and measurement equipment will be maintained by the same staff conducting the study. The performance of the test equipment will be observed during all tests, so that any malfunctions can be identified and repairs initiated with minimal impact on the test schedule. Maintenance will be performed on a scheduled basis for the real-time formaldehyde monitor, and on an as-needed basis for other equipment. For the real-time monitor, scheduled maintenance will consist of replacement of peristaltic pump tubes at an interval of one week. More frequent replacement will be implemented if necessary. Significant equipment problems during a test will be documented along with the test results, as will any corrective maintenance or replacement of equipment.

Maintenance of other equipment will include replenishment of water in the humidification system, calibration/repair of mass flow controllers in that system, cleaning of the test chambers, and repair of other equipment such as the temperature and humidity sensors and the DNPH sampling equipment. Some of this equipment is particularly important for the tests, and failure of such equipment is reason to stop testing until repairs are made. Critical equipment includes the real-time monitor, in testing of wet samples; the HPLC analysis system, in testing of dry products; and the chamber air flow control and humidification system. All study personnel have the authority to halt testing upon identification of a problem in any of these key systems.

Maintenance of a low chamber background level is also critical to the study. The chamber background will be determined at the start of all tests, prior to introduction of a sample into the chamber. Should the background exceed 10 ppbv, testing will be delayed until the chamber has been cleaned sufficiently to achieve the required background.

5. Data Acquisition and Compilation

5.1 Data Acquisition - Continuous measurements of temperature, humidity, and real-time formaldehyde will be recorded in all tests using a PC-based data acquisition system using Lotus LabTech Notebook software. This system is used in all projects that employ Battelle's test chambers, and provides data in Lotus 1-2-3 spreadsheet format for data
Quality Assurance Project Plan  
Revision: June 7, 1995

reduction. Each data channel will be sampled once every 10 minutes. The last several hours of recorded data will be displayed on the PC's screen, to allow visual monitoring of test conditions and real-time formaldehyde data.

In addition, a chart recorder will be used to display the real-time formaldehyde data during each test in which that analyzer is used. Hardcopies of all computer data files, and the chart recordings, will be placed in a primary data file for each chamber test.

Handwritten narratives will also be made in project notebooks during each test. These records will include the date, time, sample identifier, indication of chamber conditions, notes on formaldehyde levels, calibration and zero air response, and any other pertinent information. Copies of the notebook pages will be placed in the hardcopy file for each test.

The chromatographic results from the HPLC analysis of DNPH samples will be prepared using the data system on the Waters HPLC instrument. Printouts of the results will be copied and placed in the appropriate files.

5.2 Data Compilation - Product information and the results from all tests will be compiled in master spreadsheets using Microsoft Excel 5.0 software. These spreadsheets will include all pertinent information about the testing of the products. For convenience of use the size of each spreadsheet will be limited to one or more product types or categories. Included in each spreadsheet will be the product name and a unique sample number; the source from which the sample was obtained; the dates of manufacture (if available); purchase, receipt at Battelle; and testing; the lot number or comparable information; the test results for formaldehyde, and for other aldehydes; the test conditions (separate entries for the two chambers); and the calculated emission rates of formaldehyde and other aldehydes.

Separate spreadsheets will be maintained for dry and wet products, because of the different procedures required to calculate formaldehyde emissions. Duplicate samples obtained for at least ten products will be identified by a suffix to the sample number, and will be listed separately in the spreadsheets. Initial spreadsheet entries will be made for a product as soon as that sample is received at Battelle. Subsequently, additional information will be added immediately after chamber tests are conducted.

The data spreadsheets will be the primary form for recording project information, including both sample identification and test results. As such, the spreadsheets will also be the primary form of reporting the project data to CARB. Electronic and hardcopies of the final spreadsheets will be provided to CARB at the conclusion of the project, in Excel or other appropriate format.

6. Data Review and Comparison

6.1 General - As a means of assuring the quality of the data from this project, several types of reviews and data comparisons will be conducted. These range from informal observation of initial raw test data to formal statistical comparisons of final data. These planned review efforts are described below.

6.2 Raw Data Review - The initial quality control review will be inspection of the chamber test data during and immediately after each test, by the Principal Investigator and other project staff. This review will address whether the test was conducted properly and
provided sensible results. Examples of the items considered at this stage include the stability of chamber conditions; the relative emission rate of the sample relative to expectation based on the type of sample; and the comparability of data from the two chambers. For example, test results would be considered suspect if formaldehyde concentrations in the chamber at lower temperature and higher air exchange rate appeared to exceed those in the other chamber. Any problems in either the real-time or DNPH sampling will also be considered. The object of this review is an initial assessment of the acceptability of the test data.

6.3 Calibration Data Review - This effort is a review of the zero and calibration data for the real-time and DNPH methods. The purpose of this review is to assess whether the aldehyde measurements were acceptable for a given test. The items considered include the level of background response, the sensitivity indicated by calibration standards, the linearity of response, and for the DNPH method, the appearance of the chromatograms. This review step will be done during each test, for the real-time method, and during the sample analysis, for the DNPH method.

6.4 Emission Rate Review - After the test data are compiled and the product emission rate is calculated, the emission rate data will be reviewed. This process will check the correctness of the input parameters and of the calculation itself. Comparisons will also be made at this point between the emission rates calculated for each product from the tests at the two sets of conditions. Comparisons will also be made between calculated emission rates for similar product types, as a check on the data.

6.5 Duplicate Test Results - For 10 of the products to be tested, duplicate samples will be obtained and subjected to chamber testing. These duplicate tests will be conducted early in the test program, so that the reproducibility of the procedure can be evaluated and any problems rectified before other tests are conducted. A formal statistical comparison will be made between the duplicate results from both sets of test conditions. This comparison will indicate the overall precision of the chamber tests, and will be used to draw conclusions about the utility of the test results. For example, the precision observed in duplicate tests will be used to estimate how well different product classes can be distinguished from one another, in terms of formaldehyde emission rate. This will allow product categories to be ranked, or defined as equivalent in emissions, on the basis of the test data.

6.6 Method Comparisons - Formaldehyde from the DNPH and real-time methods will be compared to assess the consistency of results from the two methods. This comparison will require averaging the real-time data over the period of the DNPH measurements (30 to 60 minutes). The comparison is straightforward for the tests of dry products, because the steady state (or nearly so) conditions in those tests will assure that the formaldehyde concentrations in the chambers are uniform over the period of DNPH sampling. In testing of wet products, however, the formaldehyde concentration is expected to be decreasing somewhat at the time of DNPH sampling. In either case, averaging of the data will easily be done through the PC data system.

Results from the two methods will be compared for all tests in which both measurements are made. The degree of agreement will be assessed by linear regression analysis of the data. This comparison will also be categorized by the type of product. For example, wet and dry product tests will be considered separately, to investigate whether
other components emitted from wet products may affect one or the other method. Both the DNPH result and the corresponding averaged real-time result for each product tested will be entered in the spreadsheets described in section 5.2.

6.7 Large Chamber Comparisons - For two wood products, tests will be conducted under typical indoor conditions in Battelle's 17.3 m$^3$ chamber, as well as in the twin 1.43 m$^3$ chambers. The results of these tests will be compared as an additional check on the validity and reproducibility of the test data.

7. Assessment of Accuracy and Uncertainty

7.1 The accuracy of the overall sampling and analysis procedures will be assessed by preparing a known concentration of formaldehyde in one of the two test chambers, and determining the concentration by both the real-time and DNPH methods. This assessment will be conducted in a "blind" fashion, i.e., the operator conducting the sampling will not be informed of the target concentration. Both methods will be independently calibrated by the procedures described in section 3, and will then be used to determine the chamber formaldehyde concentration. The results of this test will indicate the absolute accuracy that may be expected in the chemical measurements.

Accuracy of the DNPH method will also be assessed by spiking DNPH solutions with known quantities of formaldehyde and the other target compounds. Those spiked solutions will then be analyzed in the same manner as are other samples. The analytical results will indicate the recovery efficiency of the various compounds in the derivatization and analysis steps, as distinct from the air sampling step.

The accuracy of the temperature, relative humidity, and air exchange rates will be assessed during normal operations by routine calibrations of the equipment or comparisons with standards. For example, a mercury-in-glass thermometer will be used to check the temperature readout, and gas flow standards will be used to calibrate the flowmeters used to set the air exchange rate. The accuracy of chamber loading rate will be assessed by measuring the size of test samples and surfaces before they are put into the chambers. This will indicate the extent to which sample sizes agree with the required sizes stated in the test protocols.

7.2 The overall uncertainty of the measured concentrations, and in turn of the calculated emission rates, will be calculated from the information on accuracy and precision of the tests. The uncertainty of the measured chamber concentrations of formaldehyde and other compounds will be estimated in a root-mean-square manner from the precision obtained in duplicate tests, and from the accuracy obtained in the test described in section 7.1. That is,

$$\% \, U = \left( \% \, A^2 + \% \, P^2 \right)^{1/2}$$

where
\[ \% \, U = \text{percent uncertainty in the chemical measurement} \]
\[ \% \, A = \text{accuracy expressed as a percentage of the measured value} \]
\[ \% \, P = \text{precision expressed as a percentage of the measured value.} \]
Quality Assurance Project Plan
Revision: June 7, 1995

The overall uncertainty in the calculated emission rates will also include uncertainties in other test factors, such as the air exchange rate, loading rate, temperature, and relative humidity. For the air exchange rate and loading rate, the uncertainties are expected to be approximately 3% and 2%, respectively, based on the DQO's for precision and accuracy shown in Table 1. However, the actual precision and accuracy found for these parameters will be used instead of these expected values, if the actual values differ substantially from the DQO's. These uncertainties will be compounded in a root-mean-square manner with the chemical measurement uncertainty, calculated as shown above.

Consideration of the uncertainty resulting from temperature and relative humidity is not so straightforward, because these parameters may affect the emission rate of a product in a non-linear manner. Furthermore, the effect of these parameters on formaldehyde emission rates is unknown, except in the case of some wood products, and is only approximately correctable even for those products. As a result, it will be assumed that the formaldehyde emission rates of all products respond to varying temperature and relative humidity in the same manner as described by Myers\textsuperscript{6} for wood products. The range of variability of temperature and relative humidity observed in the chamber tests will be used to calculate the potential variability and hence uncertainty in the formaldehyde emission rates, based on the relationships given by Myers\textsuperscript{6}.

The estimation of uncertainties in the product emission rates will not be done separately for each individual product or test. That approach would be redundant and not necessarily informative. Instead, representative uncertainty values will be calculated based on the variability of test parameters and the overall accuracy and precision found for the measurement systems. As a result, this effort will result in error limits that characterize the overall uncertainty in the tests, and that are applicable to all of the products tested. Should an individual product exhibit unusual characteristics (e.g., unusually poor reproducibility of test results for a product), then separate uncertainty estimates will be made for that product. The overall aim of this uncertainty analysis is to provide an estimate of the typical uncertainty of the study results, so that the similarity or difference of formaldehyde emission from various product types may be judged.

8. Outside Quality Assurance Data
8.1 As an additional level of quality assurance, aliquots of DNPH samples from the chamber tests will be submitted to an outside laboratory for analysis, as a quality control check on Battelle’s results. Analyses will be requested for formaldehyde, acetaldehyde, and propionaldehyde at a minimum, and if available, for the other target compounds named in section 3.1 as well. A comparison of analytical results for all target compounds measured by both Battelle and the outside laboratory will be made. The outside laboratory is Calscience Environmental Laboratories, Inc., of Stanton, California, which is recognized as a minority business enterprise by the State of California. A total of 60 DNPH samples, drawn from tests on all product categories, will be submitted to Calscience for analysis. The selection of the 60 samples will be weighted proportionally with the number of samples tested in each category, e.g., about half the samples will be from chamber tests on urea-formaldehyde wood products. Samples will be submitted to Calscience in batches, so that QA results will
Quality Assurance Project Plan
Revision: June 7, 1995

be available on the initial tests early in the program. If procedural adjustments in Battelle's
DNPH procedure are indicated by this comparison, they will be implemented as soon as
possible.

9. References

1. Interim Report on Selection of Products for Chamber Testing, prepared by Battelle,
Columbus, Ohio, for the California Air Resources Board, Project No. 93-315, March, 1995.

2. Protocol for Chamber Testing of Formaldehyde Emissions from Indoor Residential
Sources, prepared by Battelle, Columbus, Ohio, for the California Air Resources Board,

3. Protocol for Chamber Testing of Formaldehyde Emissions from "Wet" Products Used in
Residences, prepared by Battelle, Columbus, Ohio, for the California Air Resources Board,

4. T.J. Kelly and C.R. Fortune, Continuous Monitoring of Gaseous Formaldehyde Using an

5. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient
Air, EPA-600/4-89-017, U.S. Environmental Protection Agency, Research Triangle Park,

6. G.E. Myers, The Effect of Temperature and Humidity on Formaldehyde Emission from
UF-Bonded Boards: A Literature Critique, U.S. Department of Agriculture Forest Service,
Forest Products Laboratory, Madison, Wisconsin, 1984.
APPENDIX F

HCHO EMISSION/DECAY CURVES AND MODEL FITS FROM CHAMBER TESTS OF WET PRODUCTS
FIGURE F-1. LESS EXPENSIVE LATEX PAINT - TYPICAL CONDITIONS.
Model Parameters: a = 92.7, b = 6.21, c = 76.2, d = 0.490
FIGURE F-2: LESS EXPENSIVE LATEX PAINT - ELEVATED CONDITIONS.

Model Parameters: \( a = 120.0, b = 3.93, c = 86.7, d = 0.152 \)

HCHO Concentration (μg/m³)

Time (hours)
FIGURE F-3: LESS EXPENSIVE LATEX PAINT - DUPLICATE TEST, TYPICAL CONDITIONS.
Model Parameters: $a = 103.0$, $b = 7.15$, $c = 82.3$, $d = 0.576$
FIGURE F-4. LESS EXPENSIVE LATEX PAINT - DUPLICATE TEST, ELEVATED CONDITIONS.
Model Parameters: $a = 113.8$, $b = 7.88$, $c = 76.0$, $d = 0.109$
FIGURE F-5. MORE EXPENSIVE LATEX PAINT - TYPICAL CONDITIONS.
Model Parameters: a = 104.1, b = 3.56, c = 85.4, d = 0.372
FIGURE F-7. PAPER-BASED WALLPAPER - TYPICAL CONDITIONS.

Model Parameters: $a = 222.9$, $b = -3.51$, $c = 176.9$, $d = 0.363$
FIGURE F-8. FINGERNAIL HARDENER - TYPICAL CONDITIONS.
Model Parameters: \( a = 350.3, b = 3.25, c = 338.9, d = 0.787 \)
FIGURE F-9. FINGERNAIL HARDENER - ELEVATED CONDITIONS.
Model Parameters:  \( a = 322.6, b = 4.69, c = 300.4, d = 0.252 \)
FIGURE F-13. NAIL POLISH - ELEVATED CONDITIONS.
Model Parameters: $a = 24.31$, $b = 21.78$, $c = 32.12$, $d = 0.103$
FIGURE F-14. COMMERCIAL FLOOR FINISH - BASE COAT, TYPICAL CONDITIONS.
Model Parameters:  $a = 1.261, b = 4.33, c = 1.124, d = 0.435$
FIGURE F.15. COMMERCIALY APPLIED FLOOR FINISH - BASE COAT, ELEVATED CONDITIONS.

Model Parameters: a = 2.295, b = 2.67, c = 2.202, d = 0.099
FIGURE F-16. COMMERCIALLY APPLIED FLOOR FINISH - TOP COAT, TYPICAL CONDITIONS.

Model Parameters: $a = 7.901$, $b = 1.09$, $c = 7.305$, $d = 0.848$
FIGURE F-17. COMMERCIALY APPLIED FLOOR FINISH - TOP COAT, ELEVATED CONDITIONS.
Model Parameters: $a = 2.703, b = 1.58, c = 2.419, d = 0.199$
APPENDIX G

TDI EMISSION/DECAY CURVES AND MODEL
FITS FROM FINAL TESTING OF
COMMERCIALY APPLIED WATER-STOP PRODUCT
FIGURE G-1. WATER STOP PRODUCT, 70°F TEST 1.
Model Parameters: \( a = 6091, b = 13.86, c = 6108, d = 11.73 \)
FIGURE G-2. WATER TOP PRODUCT, 70°F Test 2.
Model Parameters: $a = 3219$, $b = 12.94$, $c = 3221$, $d = 9.74$
FIGURE G-3: WATER STOP PRODUCT, 80°F.
Model Parameters: a = 2929, b = 9.05, c = 2936, d = 4.12

TDI Concentration (ug/m³)

Time (hours)